

DTIC FILE COPY

(2)

The Causes of Blistering
in
Boat Building Materials
by

Thomas J. Rockett

Vincent Rose

John Florio

Alan R. Choiniere

C. Michael Trottier

Department of Chemical Engineering
University of Rhode Island
Kingston, Rhode Island 02881

Final Report

August 1985 to August 1986

submitted to

American Boat Builders and Repairers Association

and

Commandant

United States Coast Guard

DTIC
ELECTE
APR 06 1989
S H D

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

89 4 05 064

AD-A206 509

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle The Causes of Blistering in Boat Building Materials		5. Report Date August 1986	6. Performing Organization Code
		8. Performing Organization Report No.	
		10. Work Unit No. (TRAIS)	
7. Author(s) Thomas J. Rockett, Ph.D.; Vincent Rose, Ph.D.; John Florio; Alan R. Choiniere; C. Michael Trottier		11. Contract or Grant No. Grant 1501.83	
9. Performing Organization Name and Address Department of Chemical Engineering University of Rhode Island Kingston, Rhode Island 02881		13. Type of Report and Period Covered Final Report August '85 - August '86	
12. Sponsoring Agency Name and Address Department of Transportation Headquarters, U.S. Coast Guard Washington, D.C. 20593-0001		14. Sponsoring Agency Code	
15. Supplementary Notes			
16. Abstract Abstract of "The Causes of Blistering in Boat Building Materials" The highly technical document details the experimentation and research undertaken to more clearly define the nature and causes of osmotic blisters which develop in fiberglass reinforced plastics used in the construction of boats. The document is divided into the following topics: Introduction; Hull Material; Water Diffusion; Nucleation of Blisters; Blister Growth; Long Term Deterioration; Experimental Results: Blister Resistance; Net Weight Change Experiments; Permeability; Exotherm Experiment; Air Inhibition Studies; Stress Measurement Experiments; Trace Metal Analysis; Discussion. <i>Summary.</i> <i>Keywords:</i>			
17. Key Words FRP, Blisters, Boat Fiberglass, <i>Building materials</i>		18. Distribution Statement (SDW) ←	
19. Security Classif. (of this report) UNCLASSIFIED	20. Security Classif. (of this page) UNCLASSIFIED	21. No. of Pages 84	22. Price

NOTICE

This document is disseminated under the sponsorship of the Department of Transportation in the interest of information exchange. The United States Government assumes no liability for its contents or use thereof.

The contents of this report do not necessarily reflect the official view or policy of the Coast Guard; and they do not constitute a standard, specification, or regulation.

This report, or portions thereof may not be used for advertising or sales promotion purposes. Citation of trade names and manufacturers does not constitute endorsement or approval of such products.

TABLE OF CONTENTS

List of Figures.....	ii
List of Tables.....	iii
I Introduction	1
Hull Material.....	3
Water Diffusion.....	8
Nucleation of Blisters	19
Blister Growth	24
Long Term Deterioration	30
II Experimental Results	34
Blister Resistance	34
Net Weight Change Experiments	43
Permeability	54
Exotherm Experiment	55
Air Inhibition Studies	55
Microscopic Studies	58
Stress Measurement Experiments	59
Trace Metal Analysis	60
III Discussion	62
IV Summary	76
Notations	78
References	79



Accession for	
DTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By <i>per letter</i>	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

LIST OF FIGURES

Figure	Page
1. Structural model of a typical polyester resin	4
2. Water concentration in hull material	12
3. Water concentration gradient gel coat	14
4. Stress levels produced by polymer swelling	16
5. Photomicrograph of disk cracks	17
6. Micrograph of disk crack with purple halo	18
7. Scanning electron micrograph of blisters	21
8. Observed net weight changes for typical polyester composition	22
9. Osmotic forces in glass reinforced composites	27
10. Cross section of blister	29
11. Change in strength of polyester glass laminates with time	31
12. Isothermal bath for immersion studies	37
13. Acrylic test tank for single sided exposure	38
14. Effect of immersion time on weight of gel coat	47
15. Effect of immersion time on weight of gel coats	48
16. Effect of immersion time on weight of gel coats	49
17. Effect of immersion time on weight of composite	50
18. Effect of immersion time on weight of composite	51
19. Effect of immersion time on weight of composite	52
20. Effect of immersion time on weight of composite	53
21. Variation in exotherm temperature with temperature and material	57
22. Blister initiation time vs resin combination	64
23. Effect of laminate construction on blister initiation time	65
24. Surface of orthophthalic gel coat	69
25. Effect of air inhibition on surface of gel coat	70

List of Tables

Table 1 Some Common Constituents in a Polyester Glass Composite Marine Material	6
Table 2 WSM Species and Concentrations Identified in Blister Solutions	25
Table 3 Chemical Composition of Polyester Gel Coat and Laminating Resins	35
Table 4 Experimental Results	39
Table 5 Blister Severity Data for Selected Samples	40
Table 6 Net Weight Change Data	45
Table 7 Peak Exotherm Temperatures	56
Table 8 Qualitative X-Ray Fluorescent Analysis of Typical Polyester Resins and Gel Coat Materials	61
Table 9 Blister Initiation time for selected Gel Coat-Resin Combinations	63

I. Introduction

Fiberglass reinforced polyester (FRP) composites, the structural material of many small boats, are subject to a degradation phenomenon known as blistering. These blisters have been well described (1,2) and contains an acidic fluid which is under pressure (3,4,5,6). Blisters range in size from a few millimeters to several inches in diameter and normally occur near the gel coat-laminate interface (7,8,9,10,11,12) but have been observed deeper in the hull (13). Blisters are very rarely seen in the gel coat material itself. Only in one case, where two layers of gel coat were used, were blisters observed to form at the interface within the gel coat.

Good statistical information on the occurrence and severity of blisters on boats does not exist. While we have seen over 100 cases of coat blisters, there is no statistically established correlation between boat age and blister onset, severity or depth into hull. the influence of the cycle of dry land storage to immersion is not known. Reports from warmer water locations suggest the problem is more severe than in northern areas. We have seen three cases in which the hull is severely delaminated and in which decomposed resin is found more than half way through the hull. These were older boats (more than 10 years old). Estimates of the number of boats showing blisters in given localities range from 1% to 90% (12,13,14). There is a belief among many marina personnel tht the problem is more widespread now among newer boats than it was ten years ago. Again, this is unsubstantiated by reliable statistics but has been reported to us by many marina operators. Indeed, one manufacturer stated that prior to about 1980, for 10,000 boats produced they had never had any blisters reported but, since then, they have had hundreds of

complaints. The cost of repair is significant to boat owners ranging from \$10 to \$200 per foot of boat and several boats have been declared unseaworthy because of structural damage (13,14). A solution to the problem must be found to restore consumer faith in glass-polyester boats.

Data gathered in this study and evidence from past work suggest a mechanism for blister formation which is given below.

All polymeric materials have some permeability to water. The permeation rate depends on the chemical composition of the polymer, the added molecular species and the manner in which it was made. In the short-term, water moving through the hull will not attack the polymer nor will it form blisters unless it reacts with water soluble materials concentrated within the polymer network. These pockets of concentrated water soluble material (WSM) materials cause blistering. These clusters of WSM material may be present because of poor mixing during manufacture, additives to the polymer, undercuring during lay-up, air inhibition, poor "house-keeping" procedures, or because well dispersed units are concentrated by stress fields. These clusters react with diffusing water to form concentrated solutions inside the hull. The solutions are separated from the sea or lake water by the semi-permeable polymer gel coat (and resin) membrane and hence create an osmotic pressure which draws more water into the solution pocket to dilute that inner solution as required by the laws of chemical equilibria. The growing solution causes the surface to bulge, creating the blister. The solution becomes acidic and this entrapped acid causes degradation of the surrounding polymer. This process adds more low molecular weight materials to the solution thus perpetuating the process begun by LMW material. Blisters grow parallel to the hull surface and, with time, may initiate a deeper second generation series of blisters (13). It will be shown that the blisters create a stress concentration




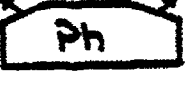


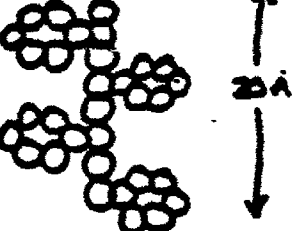
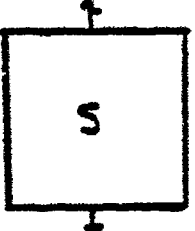

mechanism which could lead to mechanical delamination of the hull. Deeper solution pockets do not cause the surficial "blister" because of the glass reinforcement but spread laterally and attack the polymer nonetheless. This picture is partly theory which needs proof and partly well established. This report will focus on those aspects which have been proved by us or others and those areas which need more work, some of which has been conducted during this study.

The Hull Material:

While a voluminous literature exists on the chemistry of unsaturated, room-temperature curing, polyester/styrene resins, a review of all aspects of the chemistry and manufacturing methods is beyond the scope of this report. However, those aspects that are pertinent to the blister problem will be summarized. Since the first polymer/glass boats were made in the late forties and early fifties, the hull material has been a polyester/styrene/glass composite. Figure 1 shows a hypothetical diagram of the molecular structure of such a material which has been drawn more or less to scale based on the size of the atoms in each building block. The figure represents a 1:1:2:4 resin, i.e. 1 mole phthalic acid to 1 mole of maleic acid to 2 moles of glycol to 4 moles of styrene. The reactivity of the resin can be increased by increasing the number of maleic acid groups in the chain. It is impossible to show one filament of glass fiber in this diagram since the diameter of one glass filament (50,000 Å) is more than one hundred times the size of a single unit of polyester chain. The coupling agents and the binders on the glass filaments are about the same size as the polyester chain.

As shown in the diagram, there is considerable free space within the cross-linked polymer network. It is in this free space that the WSM units

MAJOR CONSTITUENTS

Formula	Molecular Shape	Representation
Glycol CH_2OH_2		
Phthalic acid $\text{C}_6\text{H}_4(\text{COOH})_2$		
Maleic Anhydride		
Styrene		
Terminal Peroxide		

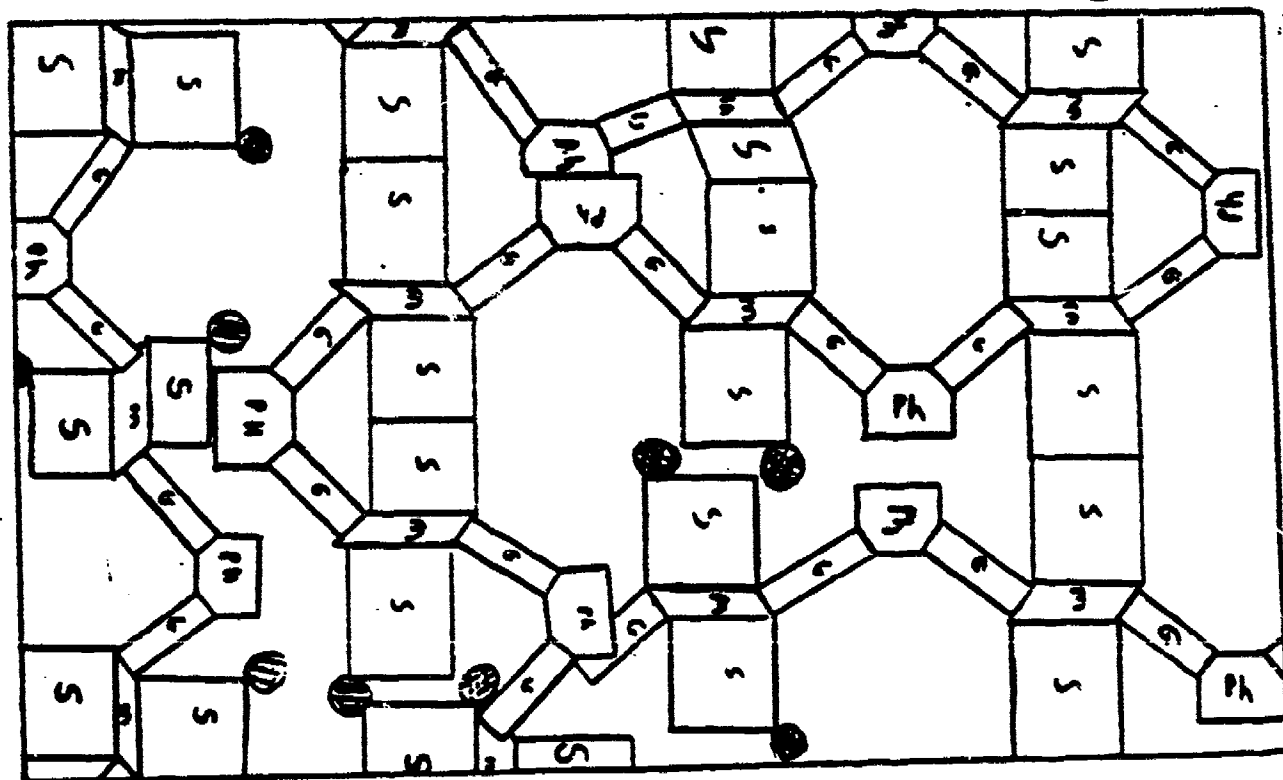


Figure 1. Structure model of a typical polyester resin.

reside, absorbed to the polymer chains by polar forces, and into which the water molecules will fit as they diffuse into the polymer. Table 1 lists the materials that can be used to make a polyester composite for the marine industry (15). Not all of the constituents will be used in a given polyester and the examples listed of each type is not exhaustive. Possible sources of WSM units are shown in the table. From 1 to 5 percent of the composite can be WSM units in a completely cured, ideal resin.

The second major source of WSM units comes from the network formers as a result of incomplete cure of the resin. In Table 1, all of the polyester groups should, under ideal conditions, be bound into a three dimensional infinite network. Three things can convert network molecules into WSM units. First, incomplete cure, caused by poor mixing, too low a mix temperature, decomposed peroxide, reaction of styrene with air, or improper catalyst package selection will mean that a certain fraction of the network formers will remain as WSM units. Second, in "cooking" the polyester, a certain fraction of material either does not react to form ester chains or forms short unsaturated chains that become WSM. Thirdly, over a period of time, chemical reactions with water or acids can break down the network (chain scission) and convert parts of it to WSM. All three of the above mechanisms can produce free glycols in a resin. Excess glycol has been shown to cause blisters (5,12).

There have been some major changes in manufacturing processes since the early fifties. Some of these were the result of design changes, some the results of material & equipment changes, and some the result of regulatory changes. In recent years, different resins, fillers, waxes, antioxidants, flame retardants, coupling agents, binders and reinforcement materials have been developed to improve the performance of the composite. Spray guns and

Table 1

Some Common Constituents in a Polyester Glass Composite Marine Material. Materials are classified as network formers (NET), low molecular weight units in the network (WSM) and stable additives (STAB).

1. Polyester Groups
 - Orthophthalic acid or anhydride (NET)
 - Isophthalic acid or anhydride (NET)
 - Epoxy and/or acrylate units (NET)
 - Ethylene glycol (NET)
 - Propylene glycol (NET)
 - Neopentyl glycol (NET)
 - Maleic acid or anhydride (unsaturated) (NET)
 - Fumaric acid (unsaturated) (NET)

A phthalic acid, a glycol and a maleic are reacted to form the unsaturated polyester. The ratios can vary from 1p:1m:2g to make a moderately reactive polyester to 2p:1m:3g for a low reactive polyester to 1p:2m:3g for a highly reactive polyester. Ordinarily a slight excess of glycol (1:1:2.1) is added to ensure termination of the chains by glycol units. Excess glycol or uncured components will contribute to WSM fraction. (WSM)
2. Cross-linking Agent or Vinyl Molecule (NET)
 - Styrene (40 to 50 weight percent) (unsaturated vinyl molecule)
 - Acrylic (only in experimental resins) (NET)
 - (Added styrene will yield a total ratio of 1p:1m:2g:4 styrene. The viscosity of the resin is largely controlled by the amount of styrene)
3. Inhibitor: (0.1-0.5%) - added to increase shelf life.
 - Quinones (WSM)
 - Amines (WSM)
4. Ultraviolet stabilizer (in gel coats 0.1-1%)
 - Benzophenones (WSM)
 - Hindered amines (WSM)
5. Colorants (in gel coat materials)
 - Inorganic pigments (1-5%) (STAB)
 - Organic pigments (1-5%) (WSM)
 - Carriers (phthalate plasticizers) (0-3%) (WSM)
6. Catalyst (initiator - added to react with unsaturated bonds and cause cross-linking - they become part of network)
 - Azo-compounds (NET)
 - Methyl ethyl ketone peroxide (1-2%) (NET)
 - Benzoyl peroxide (NET)
 - Phthalate carriers (WSM)
7. Promoter (accelerator - the true catalyst which activates the initiator)
 - Cobalt salts (octoates, naphthenates, alsynates) (WSM)
 - Anilines (dimethyl) (WSM)
 - Mineral spirit carriers (toluene) (WSM)

Table 1 (continued)

8. Reinforcement
(Mats, woven fabrics, chopped fibers)
Fiber glass - Silicate network with calcium sodium, (STAB)
magnesium and aluminum
Glass surface ions leached through long term acid exposure (WSM)
Aramid Fibers - Carbon Fibers (STAB)
9. Coupling Agents (bond formers between the polymer and the glass)
Various silane compounds. (STAB)
Titanates, Mordants (chromium compounds) (STAB)
Reaction products from a long-term acid exposure (WSM)
10. Sizing (lubricants and handling agents (WSM)
added during fiber glass manufacture)
Starches and emulsions. Most are burned off before composite manufacture.
11. Binders (added to hold mats & filaments together)
Polyvinyl acetate emulsions (WSM)
Polyester powder (STAB)
12. Thixotropes - (added to prevent runoff of resin)
Ultrafine SiO₂ (STAB)
Clays (STAB)
13. Fillers (added to reduce cost)
Clay (could cause swelling by water absorption) (STAB)
Talc (could cause swelling by water absorption) (STAB)
Limestone (could cause swelling by water absorption) (STAB)
Ions leached from fillers (WSM)
14. Waxes (added to prevent air inhibition and as mold release (STAB)
agents)
Will not interact with water but can cause localized low strength zones.
15. Wetting Agents (added to lower interfacial energy and enhance resin wetting of glass)
Oleates, stearates, emulsifiers, surfactants (possible WSM)
16. Flame Retardants
Halogenated compounds (WSM)
Aluminum hydrates (STAB)
17. Impurities (can enter at any stage in which new materials are added)
Water, Benzene, Aldehydes, Ketones, etc. (WSM)
Dirt, dust, wood chips, lint. (WSM)

chopper guns also have come into widespread use. Catalyst compositions were altered to satisfy the Department of Transportation shipping regulations of the late 1970's. These regulations reduced the percent of active oxygen in the MEKP catalyst from 11% to 9%. OSHA regulations issued in the early 1980's may affect resin compositions. Oil prices could also alter the percent of fillers used or the source of the organic components. If statistical information on blister frequency were available, these data could be correlated with such changes to isolate cause and effect relationships.

Another unanswered question concerns the curing mechanism of the hull material. We assume that, during cure, all WSM units are trapped within the growing network. If during lay-up, polymerization begins at the mold surface and moves outward, the WSM could be pushed ahead of the moving gel boundary and concentrated at the free surface. In addition, oxidation of the surface by air inhibits cure by breaking up styrene molecules. These materials might be dissolved in the next layer of resin and upset the distribution of WSM locally.

A certain level of WSM units is essential to a well designed resin, and does not result in a composite of low blister resistance. However, if they are concentrated beyond normal limits or if they are concentrated at given locations, short term blistering will result.

Water Diffusion

There are two ways that water can move through a polymer. If there are small channels or pin holes in the plastic, liquid water (as a distinct phase) can flow through these holes. the permeation rate, i.e. the amount of water (gms, c.c. or buckets) that move across 1 square foot of the hull in 24 hours, for a given hull thickness, is determined by the size of the holes in the

polymer and the difference between the amount of water on both sides of the polymer. The amount of water is measured as a concentration (partial pressure, weight percent, mole percent or activity). While this type of flow transport may be possible in some polymers it can never create osmotic pressure. For osmotic pressure to build, water must be able to move inward, but WSM must not be able to move in the opposite direction. Osmotic pressure in hulls is generated by the concentration difference between two solutions separated by a polymer membrane. The easiest way to equilibrate the concentration of the pocket of the WSM solution and surrounding water is to have the WSM move into the water. A membrane with pores and holes would allow this to happen. There would be little resistance to the movement of WSM and no osmotic pressure could build.

The type of transport that is more important to understanding blistering is molecular diffusion. Here, water molecules leave the liquid phase (sea water) and become dissolved in the free space of the polymer. The water molecules jump from one space to the next open space moving from outside the hull, through the polymer and eventually become constituents of the air (relative humidity) inside the boat.

In molecular diffusion the permeation rate (the rate of water movement) is related to the resistance of the water molecule to move from one site to another and this is determined by the absorption forces acting on the water molecule by atoms in the polymer network and the WSM units. Also controlling the rate of water transport is the difference in the amount of water at any two points in the hull. As D is a measure of the resistance to movement, this concentration difference acts as the driving force to cause movement of water. As the concentration difference across a given depth into the hull increases

(if the resistance remains the same) water moves faster. As the amount of water at the two points becomes the same, water movement stops.

The movement of water can be expressed in a series of mathematical laws which take the following form:

J (Flux or rate water is transported through hull) = D (Diffusion coefficient which is inversely proportional to the resistance to water movement) $\times dc/dx$ (water concentration gradient or driving force for movement).

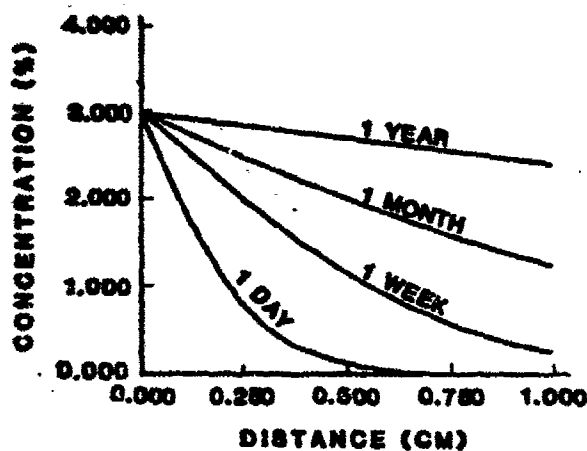
Furthermore the change in amount of water at a point in the hull as a function of time also can be determined by the change in the flux (J) at the point. This takes the following form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} (J) = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right)$$

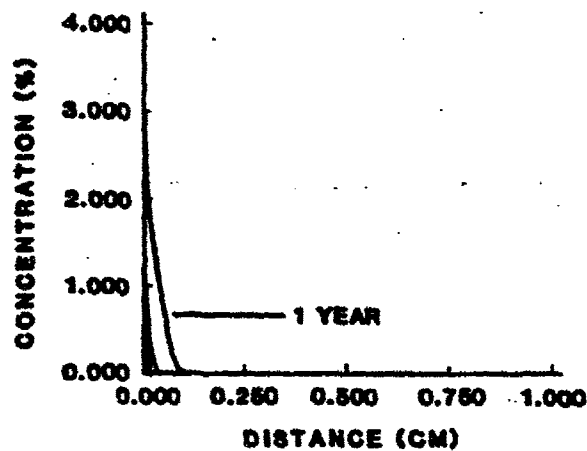
These two expressions are known as Fick's Laws and water movement which obeys these laws is known as Fickian diffusion (16). In order to solve these equations another important piece of data must be obtained for hull materials. The water gradient is controlled by how much water can dissolve in the polymer, i.e. for a given polymer volume, the number of free space sites that a water molecule can occupy. This value is known as the solubility of water in the polymer (S) or the saturation level of water. Just as D differs for different polymers, so does S . We assume that as soon as a polymer is placed in water the open spaces for water at the surface will be filled instantly and

from that point on, the water gradient changes as diffusion takes place. Figure 2 shows water profiles which were generated using a computer model. The curves represent concentrations of water at different depths for various times and make use of diffusion coefficients that have been measured for a cross-linked polyester resin. All four profiles are shown for a constant temperature (72°F). The water movement is greatly affected by temperature since D changes with temperature and pressure (17). Water will move roughly twice as fast into the hull for every 18°F increase in temperature.

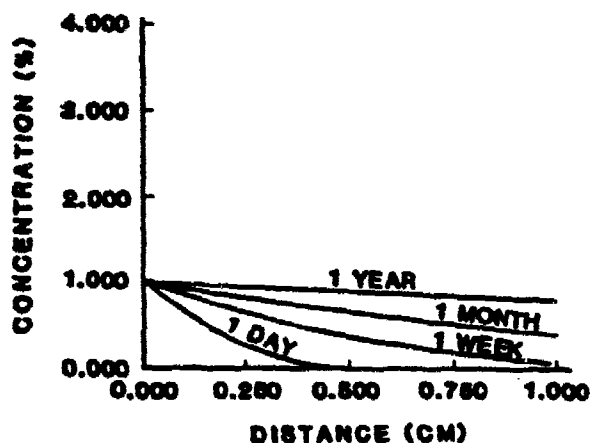
The diffusion coefficient, D, and the saturation level, S, is different for each polyester composite. The amount of filler and glass lowers D and S by eliminating water sites in a given volume of composite. The chemical entities in the network (see Fig. 1) and the water affinity of the WSM affect D by determining how strongly a water molecule is held by absorption forces. Hence, ortho, iso and vinyl polyesters will all have different S and D values. A WSM glycol unit which bonds to water will tend to lower the D value but increase the S value of the composite. Finally, the degree of cross-linking is extremely important since it effects both D and S. The degree of cross-linking is determined by both the number of unsaturated sites present, which is controlled by amterial selection, and the number that actually form which depends on the degree of cure. A highly cross-linked resin will have few open sites available for water molecules (low S) and it will be more difficult to move them from one site to another through the rigid network (low D). This will give case IV on Figure 2. If the same polymer is undercured it will have a more open structure and higher values of S and D value. Hence a difference in cure during manufacture of laminates using the same resin will alter the water transport properties dramatically.



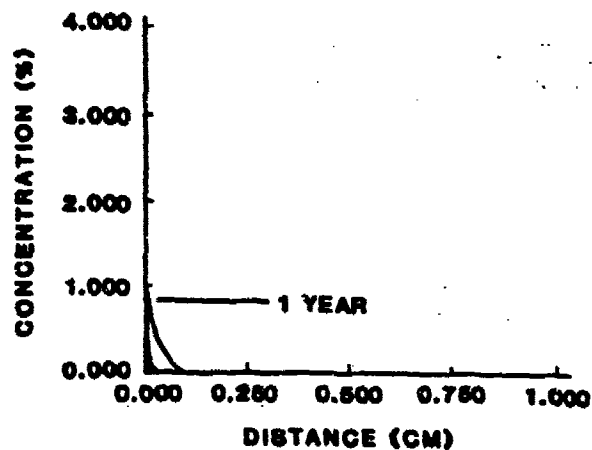
Case I: $D = 1 \times 10^{-3} \text{ cm}^2/\text{hr}$; $S = 3\%$



Case II: $D = 1 \times 10^{-7} \text{ cm}^2/\text{hr}$; $S = 3\%$



Case III: $D = 1 \times 10^{-3} \text{ cm}^2/\text{hr}$; $S = 1\%$



Case IV: $D = 1 \times 10^{-7} \text{ cm}^2/\text{hr}$; $S = 1\%$

Figure 2. Water concentration in hull material at various times for different polyester properties. Constructed from computer modeling of the polyester water system. Temperature remains fixed at 72°F

In Figure 2, we have considered only a single material for the hull laminate. Once we add a gel coat to the hull, a multiple layer model must be used. Figure 3 shows the effect of a gel coat on the water concentration gradients. Several things become obvious. In many cases, (c,d,e,g,h, etc.), there is a discontinuity in water content at the gel coat laminate interface. If a discontinuity does not exist, a change in gradient will exist except in the cases where the gel coat and laminate have the same resin base (a,f,k,p).

The amount of water present at any given spot causes swelling of the polymer. The water molecule in the site pushes apart the resin and stresses the network bonds. Our measurements, and literature values show the resin can swell as much as 10 percent by volume and this, again, is greatly affected by the degree of cross-linking (18). Stresses are generated by differential swelling. If the entire hull swells uniformly, no stress will result. However, if one layer swells and the adjacent layer doesn't swell, but is bonded to the first through the polymer network, the adjacent layer will be pulled apart (put in tension) by swelled layer. The level of stress that is generated will be determined by the water gradient, (and discontinuities) and not by the absolute water present. The lowest gradients during diffusion will be related to low S values and high D values as in case III of Figure 2, where not much water gets in and it moves quickly. The worst case for stress buildup will occur in cases II where lots of water is absorbed (high S) and it moves very slowly (low D), therefore keeping the polymer stressed for prolonged periods. Several experiments have shown that orthophthalic resin are of this type. When combining the gel coat and the resin, and assuming the two have about the same flexibility (stiffness or modulus), the worst cases for stress are where there are large step down discontinuity at the interface which produce high stress. Once the stress exceeds the failure strength of

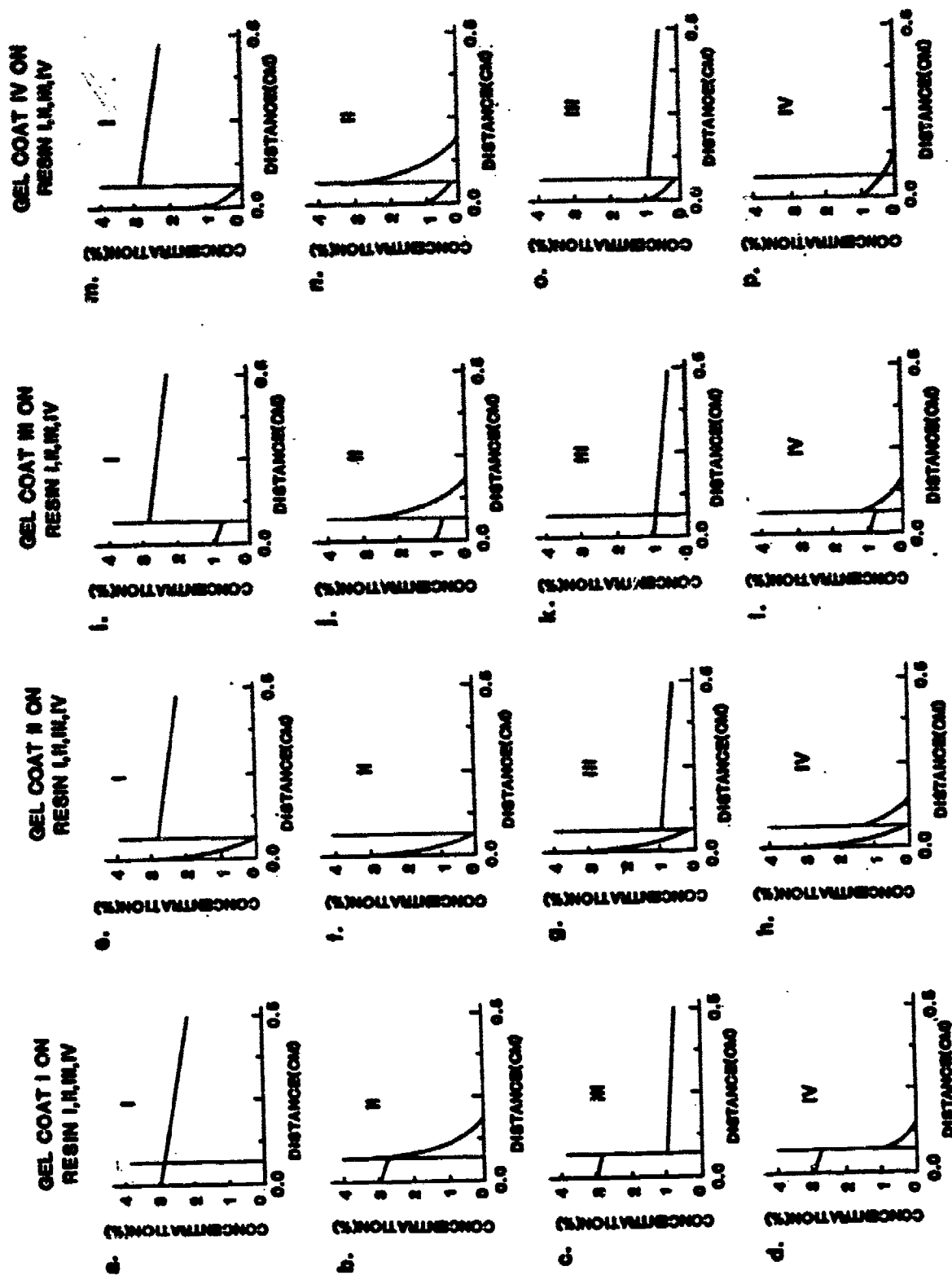


Figure 3. Water concentration gradient in gel coat.

the polymer, the step down discontinuity at the interface produces high stress and forms stress cracks, also known as disk cracks and penny cracks. Figure 4 shows the relationship between water absorption and stress build-up. Figure 5 is a photograph of disk cracks formed in a resin.

Note that the maximum in tension lies under the surface and ahead of the diffusing water front. The stress is transient. The maximum tension will move inward and decrease in magnitude as water diffuses. If the resin has high strength (well cured, highly cross-linked, reinforced with glass) it can survive the stress and not crack. If cracking does take place, the disk crack constitutes a vacuum. Any local WSM will be drawn toward the freshly opened crack to increase the pressure. This is a mechanism for concentration of WSM units in the vicinity of the crack. Figure 6 shows a localized concentration of cobalt around a disk crack. Our conclusion is that stress cracks can create blister centers.

The stress build-up can also have an effect on water transport and may lead to non-fickian diffusion. As the result network goes into tension, the free sites are opened and water can move into the zone faster than predicted by Fick's Law. This can lead to a diffusion profile with a sudden drop which is characteristic of an advancing precipitous water front. To establish the shape of the water profile, water concentration measurements at different depths at given times must be measured.

As water moves through the resins, air bubbles which are always present do not fill up with water. The water content in the air undoubtedly increases but there is no chemical driving force to create a liquid phase in the bubble. We have observed this lack of water in the bubbles repeatedly. While water diffusion does not cause blistering, it is the first step in leading to the sequence of events which result in blisters.

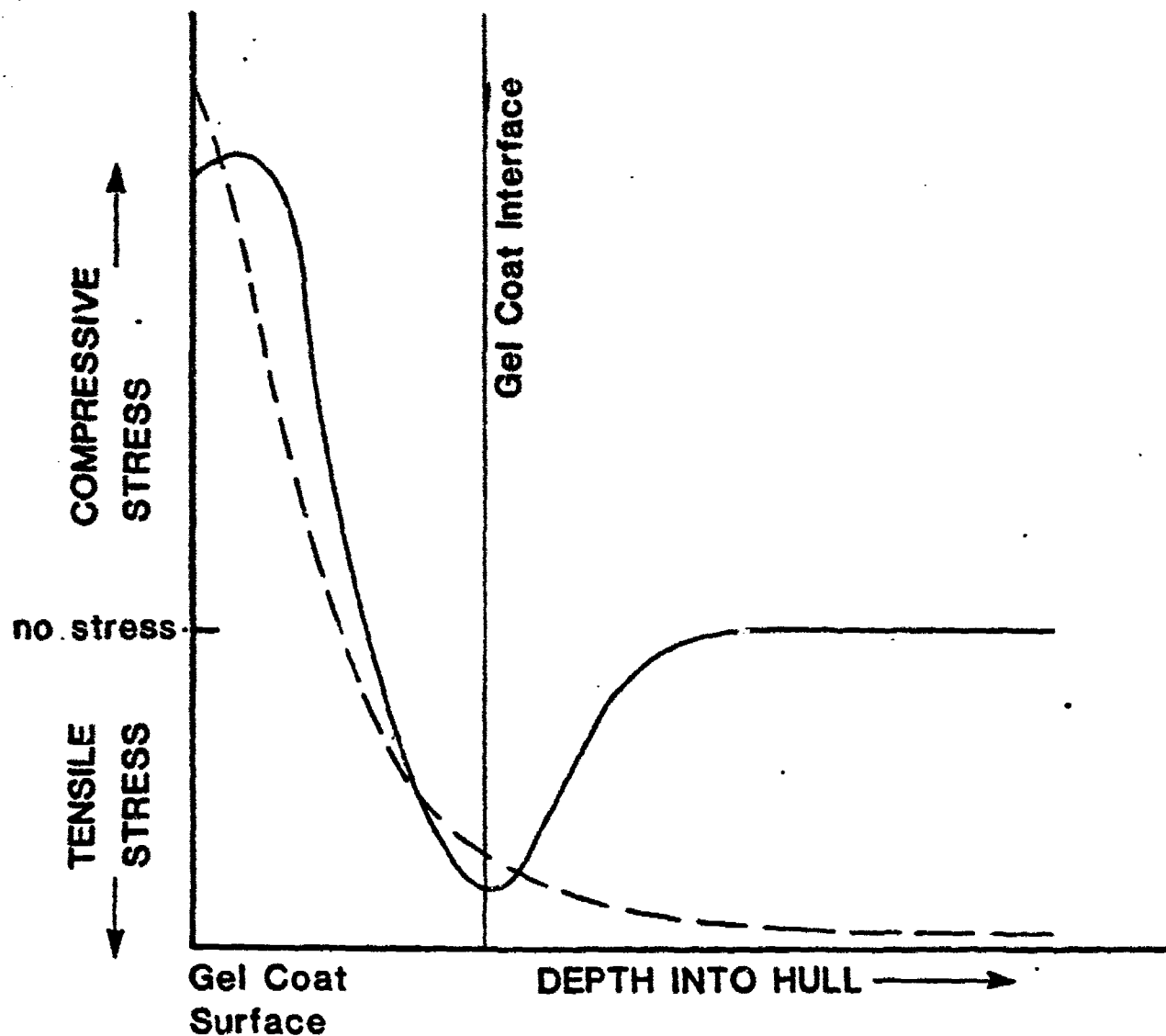


FIGURE 4. Sketch of a laminate cross-section.

The amount of water absorbed by the polymer is plotted with a dashed line. The absorbed water generates swelling stresses which are indicated by the solid line.

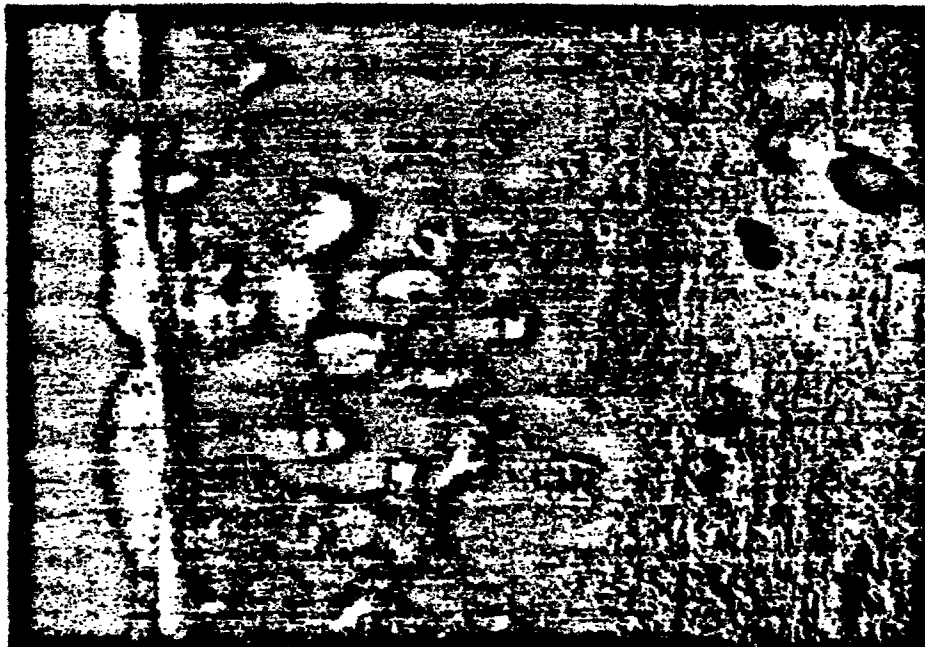


Figure 5. Photomicrograph of disk cracks (stress cracks) in a polyester resin. They are circular internal cracks which are about 1 mil in diameter.



Figure 6. Micrograph of a disk crack surrounded by a purple halo, which is caused by a high cobalt concentration. The cobalt from the promoter salts was drawn into the vacuum associated with newly opened disk cracks.

Nucleation of Blisters

The next step in blister formation is the reaction of the diffusing water with a cluster of WSM units to form a droplet of solution. The implication is that in order to form a blister, many WSM units must be concentrated in one spot. WSM evenly dispersed in a polymer network will interact with water molecules but once a shell of water molecules has surrounded the WSM, this hydration complex can not move through the polymer network. To form a solution many WSM units must be present at one place before the water molecules arrive by diffusion.

Table 1 lists the constituents in a resin which can play the role of WSM. How they become concentrated at a given spot must now be considered. Ways included undercuring, poor mixing of additives, contamination of reinforcement materials etc. Undercuring either by not using enough catalyst or promoter, by using the inappropriate catalyst or promoter or by not achieving adequate cure temperature can produce regions in the polymer filled with glycol terminated polyester units not bound into the network. These units can react with water to form the solution droplet which leads to blistering.

Poor mixing of the catalyst materials with the resin can also produce regions of undercure. Either because of poor mixing in a "hot pot" system or malfunctioning or misuse of a spray gun, a resin can contain zones in which the catalyst is highly concentrated and zones in which it is underconcentrated. Both sites can nucleate blisters.

A third mechanism of WSM concentration is related to the stress cracks discussed above. When the disk crack opens, a vacuum is created within the crack. WSM units uniformly dispersed in the surrounding network are drawn into the open crack. As the water molecules arrive at the crack, they are

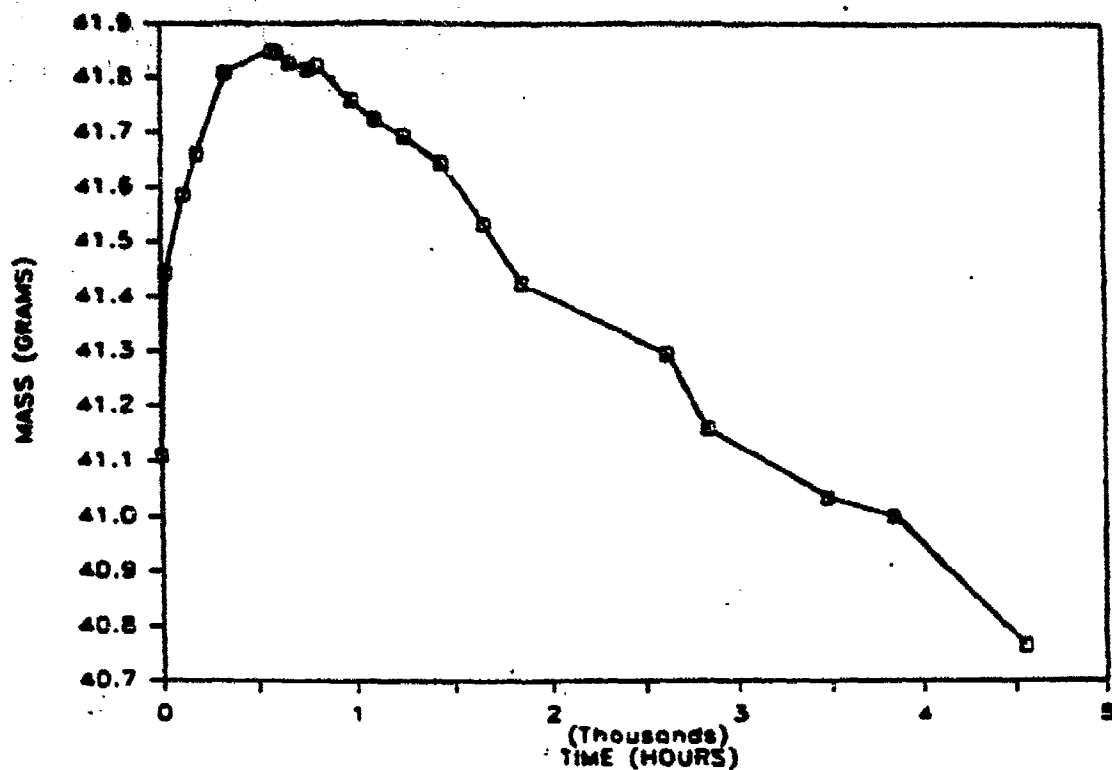
drawn into the crack by the low pressure inside the crack. Water reaction (hydration) with the now concentrated WSM create a solution. This is shown in Figure 6. The purple color is caused by cobalt enrichment inside the disk crack. Figure 7 shows a blister which was nucleated at a disk crack and grew by osmotic cracking of the resin.

The mobility of the WSM units through the polymer network is extremely important in determining its role in the blistering process. The mobility is determined by the size of the WSM unit, the size of the spaces in the network and the strength of the polar forces between the network and the WSM. If the unit is highly mobile, it cannot cause blisters. Osmotic pressure can only be generated in the presence of a semi-permeable membrane which is one that will allow water to diffuse inward but will not allow WSM to diffuse outward. Movement of species in a polymer is controlled by concentration differences. Movement is always from the high concentration zone to the low concentration zone. The movement is often facilitated by water molecules since they break the bonds between the network and the WSM units. If a region of WSM concentration exists and begins to react with diffusing water to form a solution, osmotic pressure will not build if the units can move through the polymer network and diffuse into the water surrounding the polymer. This process is known as leaching and will prevent blistering. The results of one of our weight change experiments is shown in Figure 8. The loss of weight after 600 hours is the result of leaching of WSM material from the polymer network. We have also identified materials in the test tank water which are leached from the polymer network. A polymer can contain some leachable units and still blister if other WSM cannot be leached. If all WSM can be leached, the network, while blister resistant, may be so poorly cross-linked that



Figure 7. Scanning electron micrograph of a blister under a gel coat showing the interaction of the growing blister with stress cracks. The white phase is a glass fiber. The circles are air bubbles. Gray phase is resin. Black regions are the blister and the stress cracks. Gel coat is seen above the blister.

SAMPLE-3B



SAMPLE-7B

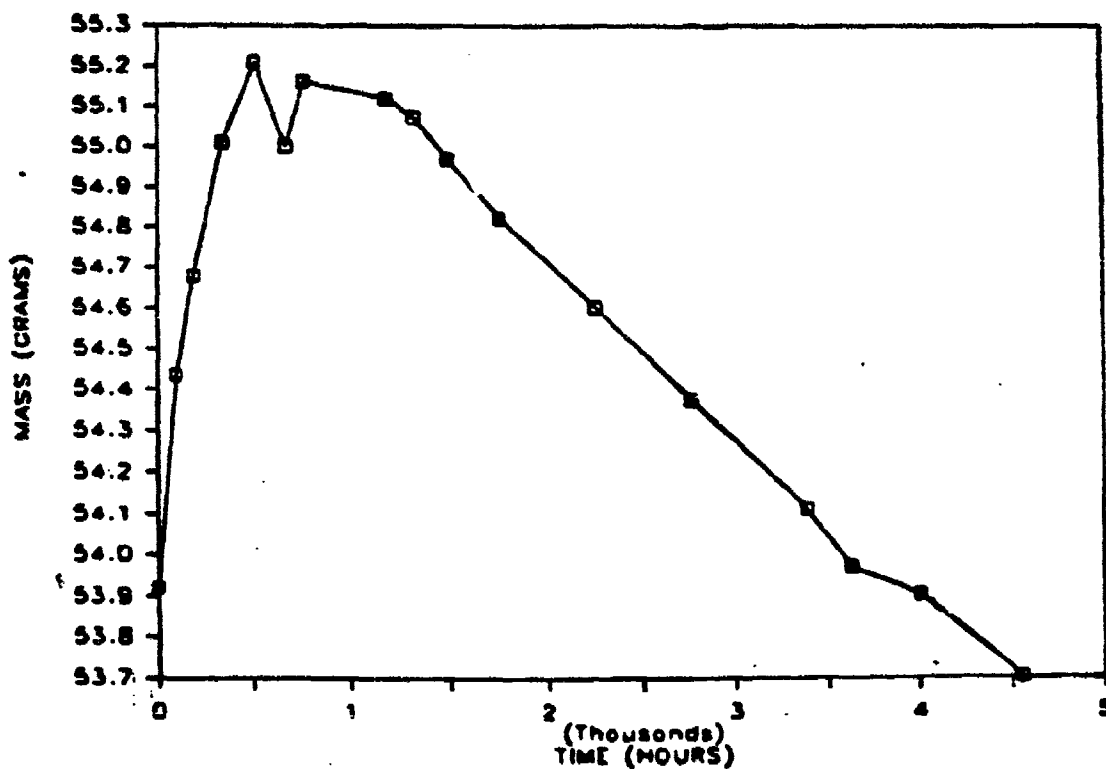


Fig. 8. Observed net weight changes for typical polyester composites. Samples were exposed to 65°C distilled water on all surfaces.

excessive water absorption may deteriorate the polymer network after prolonged exposure.

When water molecules encounter WSM molecules (or ions) there are five interactions that may occur. They are association, hydration, solvation, ionization and reaction. The chemistry of the WSM molecules, that is, the atoms that make them up and the way they are bonded together, determines which of the interactions occur. If a molecule such as styrene, which is essentially insoluble in water, occupies a space in the network and a water molecule enters that space, the two will coexist in association. Hydration will take place if the molecule forms polar interactions (weak bonds) with the water molecule. A shell of water molecules will build up around the WSM. The number of water molecules will range from 4 to as many as necessary to complete the shell which in turn depends on the size of the WSM, the space available in the network and the ease with which the polymer network can be pushed aside. This swelling is a function of how tightly the resin is cross-linked. Solvation takes place when the water molecules continue to build shells around the WSM until a small droplet of liquid is formed and the WSM is free to move within the new solution droplet. This depends on the affinity of the WSM for water. The fourth interaction is ionization. If WSM units contain charged atoms (ions) in its structure, the water molecules can separate the positively charged units from the negatively charged units. Cobalt ion (Co^{++}) bound to an octoate molecule can be separated so that the solution becomes an electrolyte which is a solution that can carry charged particles. The most common and potentially dangerous to the resin network is the ionization of an acid. The hydrogen proton (H^+) is separated from the rest of the WSM molecule and is now free to move and attack the resin network. Finally, chemical reaction may occur. The water molecule causes a break in

chemical bonds in the WSM and a new molecule (or two) forms, with the water molecules now built into it. This reaction-formed WSM can either form hydrates or solvates.

Association and hydration result in water pickup by the resin and swelling but not osmotic pressure. Solvation or reaction plus solvation can result in osmotic pressure. One WSM unit in a droplet of solution will not cause osmosis because the single unit creates a very dilute solution which does not require more water to lower the solution concentration. If, however, a cluster of water soluble WSM units are present in one area, the water molecules will form a concentrated solution. The concentration of sea water is roughly one WSM unit (sodium or chloride ion) per 100 water molecules. If the first drop of blister fluid that forms has 4 WSM units for each 100 water molecules, the laws of chemical equilibrium demand that the two solutions become equal in concentration. If the WSM cannot diffuse through the network, 300 more water molecules will be drawn by osmosis into the blister solution. Now a space problem exists since there is not room for the 300 molecules. The demand for chemical equilibria still exists and those drawn in molecules begin to build an osmotic pressure, pushing in all directions against the polymer network, and setting the stage for blister growth.

Table 2 lists the materials (WSM) which have been found in boat blister liquids (3,5,19). The acids, phthalic, acetic and maleic, contribute to the acidity of the blister solutions. All blister fluids, with the exception of the fluid in small coating blisters which form between gel coats and paint layers, are acidic and with age approach of pH of 3, which indicates that it is a corrosive acid.

Blister Growth

Table 2

WSM Species and Concentration Identified in Elister Solutions and
Possible Sources of These WSM Units. (3,5,19).

<u>Substance</u>	<u>Relative Amount</u>		<u>Source</u>
	Peak Size	moles/cm ³ × 10 ⁻² or ppm	
Glycol			Unreacted starting material;
1,2 propylene	Very Large	3.6-3.6	Degradation product
Diethylene	Very Small	1.4-6.6	
Phthalic Acid	(ppt out as white solid)		Unreacted starting material; Degradation product.
Styrene	Fairly Large	0.018-0.096	Unreacted cross-linking monomer
Benzaldehyde	Medium	0.24-0.61	Decomposition product of Styrene monomer in air; hydrolysis (H ⁺) product of Styrene
Acetic Acid	Medium	0-0.76	Polyvinyl acetate (glass binder or size)
Acetone			Solvent
Methyl Ethyl Ketone	Medium		Initiator
Toulene	Very Small		Impurity in Styrene Monomer
Xylene	Minute		"
Ethyl Benzene	Very Small		"
Benzene	Very Small		"
Sodium		15-450ppm	Fillers; fiberglass
Potassium		55-570ppm	" " or promoter
Calcium		1350-7600ppm	" "
Magnesium		100-2000ppm	" "
Zinc		50-125ppm	Promoter
Aluminum		425-2850ppm	Fillers; fiberglass; fire retardant
Iron		50-130ppm	Fillers
Cobalt		110-210ppm	Promoter
Copper		8-20 ppm	Promoter

As stated above, once the acidic blister solution has been formed and osmotic pressure develops, a uniform force is applied to the surrounding resin as shown in Figure 9. The network bonds around the growing solution are stretched in tension and, in that activated state, are subject to attack at the ester linkages by protons (H^+) in the solution. By breaking these bonds, a crack begins to grow from the droplet outward. This crack will grow in the direction of lowest strength of the composite. The lowest strength direction is perpendicular to the reinforcing glass fibers - the one direction that is not reinforced. The ester attack, which is known as chain scission because the network chains are cut, releases a unit from the network structure into the blister solution. Hence a glycol, a phthalic acid or a fumaric acid leaves the network and becomes WSM in the solution and thereby increases the concentration of the blister solution. Cracking releases the stress on the polymer network, but at the same time exposes fresh resin to attack. The material formed increases the concentration of WSM units thus demanding more water molecules in the solution. More water is added and osmotic pressure builds again until the resin cracks again. As the crack grows, more and more resin is exposed to the acidic liquid and more acid attack (protonation or chain scission) takes place. This process causes the top of the blister to be raised pushing the gel coat outward forming a blister on the gel coat surface. Note that, once started, the process is self-perpetuating. Essentially, blistering is a form of environmental stress attack which is the most severe attack to which a polymer can be exposed (20). Microhardness tests, which were performed on resin adjacent to blister pockets, show a deterioration of the strength of the polymer. Indeed, around several blisters, there was a zone of "punky" resin which had no strength at all. This is due to prolonged attack of the ester linkages which breakup the network cross-linking so that the

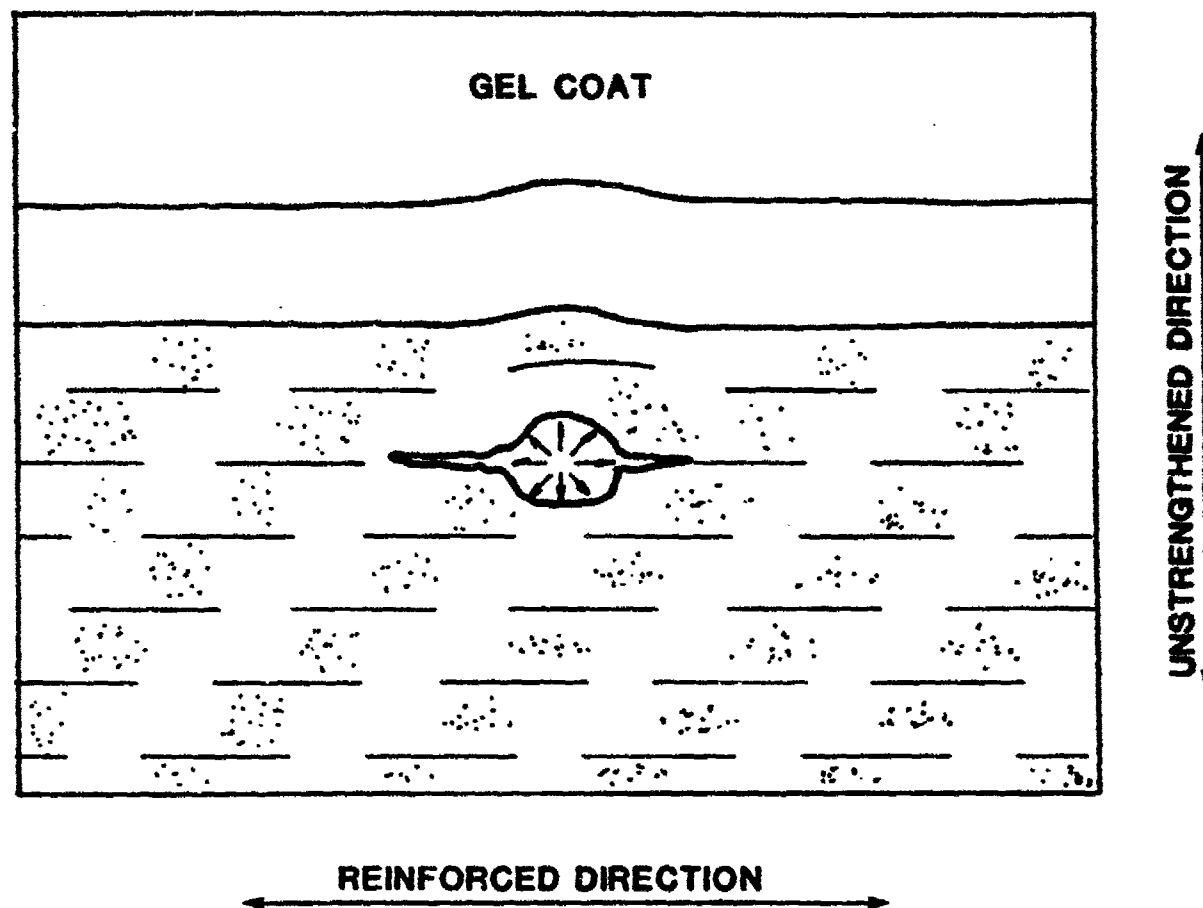


Figure 9. Sketch showing osmotic center and direct direction of osmotic forces in glass reinforced composites. Blister growth proceeds by osmotic cracking perpendicular to the unstrengthened direction.

resin becomes dissolved in the blister fluid. Figure 10 shows a cross-section of a blister taken under the microscope. The darkened resin at the crack tip and in areas adjacent to the blister show evidence of polymer deterioration. It is worth noting that a glass chopping spray gun may have an advantage over chopped strand mat or woven roving. The advantage is that not all of the reinforcement lies parallel to the surface. Fibers at an angle to the surface give some reinforcing strength (and therefore resistance to blister growth) in the direction in which blisters grow. Unfortunately, our studies show that most chopper gun roving has more soluble binders than other types of reinforcement.

Some blisters crack the overlying gel coat if the gel coat has low flexibility. When this happens, the blister solution mixes with the water from outside the hull and dilutes the blister solution. Then the sequences of water diffusion, interaction with WSM and nucleation of a blister at a deeper level can begin again unless the resin beneath the ruptured blister is so porous that WSM is leached out the resin. In this case, reblistering will not occur, but water take-up by the hull may be excessive.

If the blister does not rupture the gel coat, can a second generation of blisters form (perhaps many years later) at a deeper site in the hull? We have seen blisters in a single hull cross-section at several different depths in the hull.

All of our evidence to date indicate that blistering is continuous if WSM concentrations exist through the hull. Sooner or later, depending on water permeation rates and the length of time the boat remains in the water, blisters will form at deeper levels as the near surface ones continue to grow. Note that if the WSM materials is concentrated at a particular depth (just below the gel coat, for instance) then this would be the only level at which

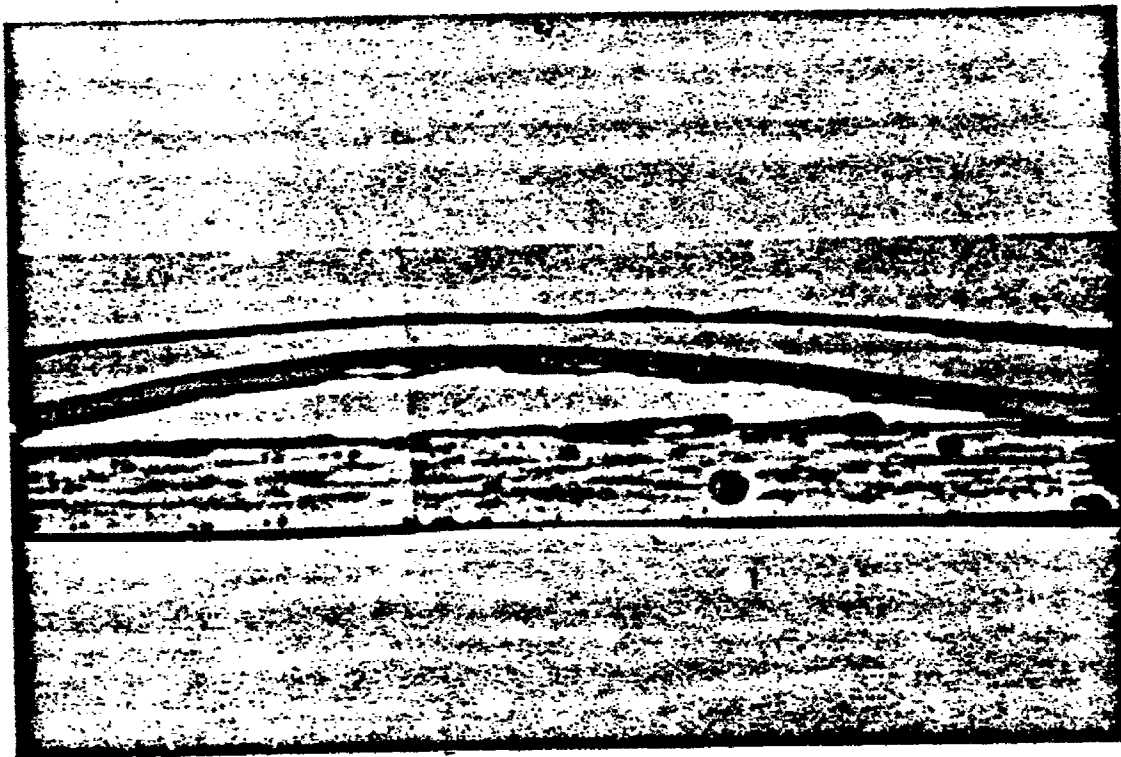


Figure 10. Cross-section of blister showing crack growth and deterioration of polymer at crack tip and the surface exposed to the blister solution. Length of the blister is one inch.

short term blisters will form in the hull. Similarly, if any other mechanism concentrates WSM at a particular level, blistering will take place at that level.

Long Term Deterioration

If the strength of a polyester/glass composite is measured after soaking in water for prolonged periods, the strength falls as water diffuses into the material. Figure 11 shows the strength-time curve for a polyester. This loss of strength takes place without blister formation (21).

There are several mechanisms which account for the strength loss. Water diffusing into the free space of the polymer acts as a plasticizer. This means that the water molecules absorb on the polymer network chains and break the polar forces between units of the network. Thus as the polymer swells the network becomes less rigid and will deform at a lower stress.

Ester linkage attack, chain scission, is the second mechanism that lowers strength. As water molecules diffuse inward they interact with WSM units to ionize acid groups. The polymer swells and the bonds in the network are stressed. The ester linkages joining the acid and glycol units are then subject to attack by the protons (H^+) and network bonds break causing strength to decrease.

Hydrolysis and leaching of WSM can also reduce strength. Some of the WSM units are attracted by polar forces to the polymer network chains. the WSM units acts as a weak cross-link between chains. When these are hydrolyzed and leached the network is weakened. Side groups, clusters of atoms that are bonded at one site to network chains, prevent network motion because of their bulk. If these are removed, the chain can slip when stress is applied. This reduces strength.

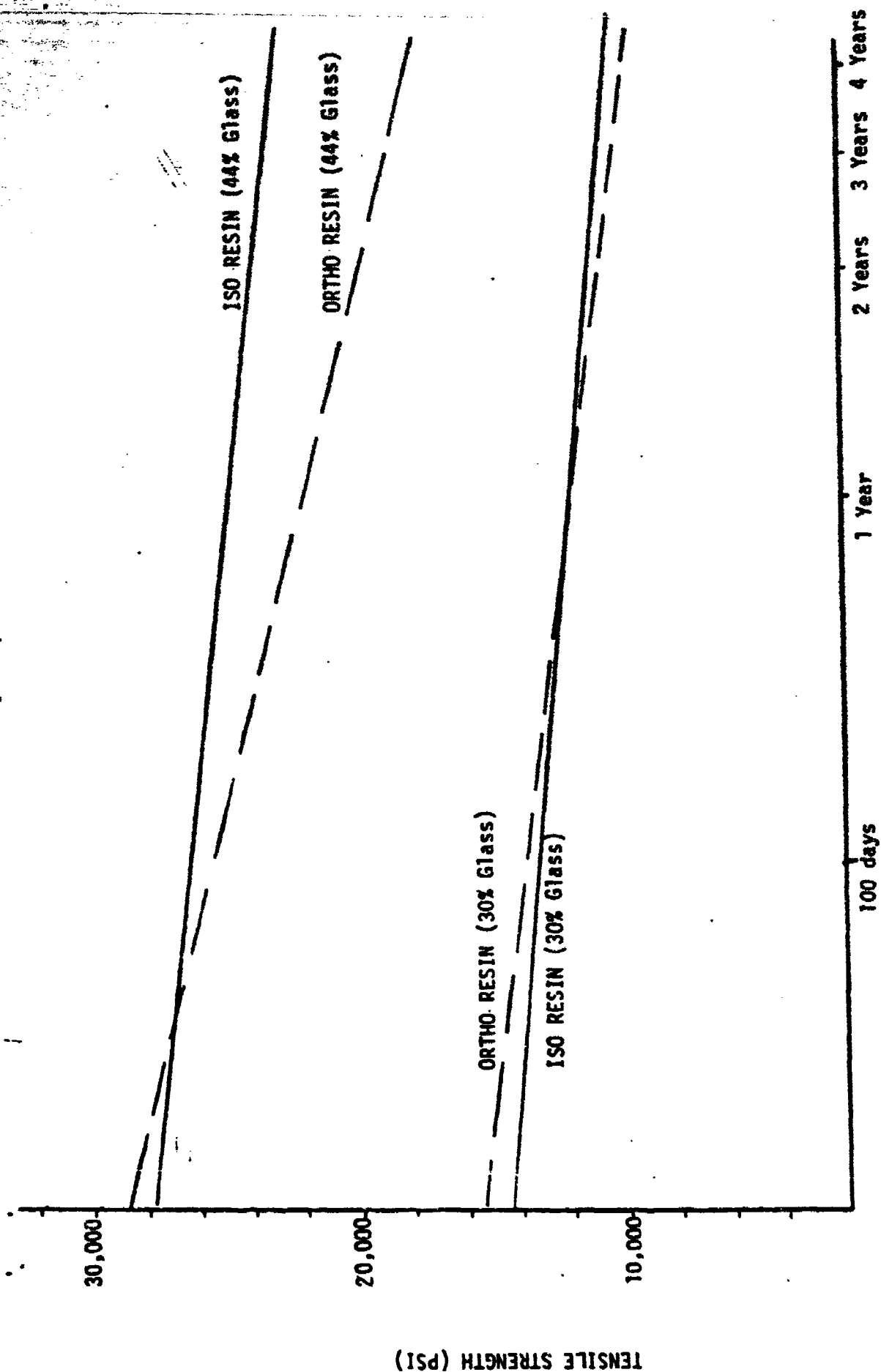


Figure 11. Strength of degradation of iso and ortho polyester glass laminate as a function of soaking time in water at 30°C (after Norwood (721)).

In order for the glass fibers to reinforce the polymer network, the glass surface must bond to the network. This is accomplished with coupling agents which are molecules which bond on one end to the glass and at the other end to the polymer. If these molecules interact with water, the coupling bonds can be broken. When stress is applied to the composite, instead of the force being transferred from the network to the rigid glass, the polymer can slip past the glass. This also weakens the composite.

The formation of hydrogel zones is a type of localized solvation. Clusters of water molecules become acidic by breaking network bonds. This opens the zone to more water ingress and large units of the network break off and become surrounded by water. With time, a zone of hydrogel forms in the network. This unit has no strength and deforms freely under applied stress.

In a composite which blisters, all of the strength limiting processes-plasticization, chain scission, leaching, glass debonding and hydrogel formation - take place adjacent to the blister. In addition to these processes, blisters weaken composites by acting as internal stress concentration. Any crack in a material has the effect of intensifying an applied stress at the tip of the crack. The degree of concentration of the stress depends on the crack length and the radius of the crack tip. If a stress on a hull is produced by wave action or sail stays and is 5000 pound per square inch, the stress at the tip of a crack can be 50,000 psi if the stress concentration factor, K , is 10. A K value of 12 was calculated for the blister shown in Figure 10.

Applied stresses concentrated at blister edges will lead to propagation of cracks from the blisters out into the laminate. As this type of delamination occurs, blister fluid will flow into the open delamination crack and begin to

interact with the freshly exposed resin, building osmotic pressure and setting the stage for further delamination.

Again, all of the strength deteriorating processes are both temperature and immersion time dependent. Blister-free polyester/glass composite boats that are thirty years old are frequently encountered. With a more complete understanding of the blistering process, all fiber glass boats could be constructed so that blistering will be minimized.

II. Experimental Procedures & Results

Blister Resistance

In order to decide which commercially available materials are best for hull manufacture and which parameters reduce blister susceptibility, a variety of test specimens were made and tested during this study. Some were made from pure resins, others were fiber glass reinforced resin while most were gel coated fiber glass reinforced laminates. All of the panels were made by hand lay-up techniques, using either brushed and sprayed resins, following standard manufacturing techniques. The typical panel, made on a waxed glass mold, was 2'x2'x1/4". Table 3 lists the materials used and specifies a number for each material. In most samples, polymerization was initiated using methyl ethyl ketone peroxide according to manufacturer's instructions. One set of samples was initiated with BPO.

Typically, 20 mils of gel coat containing 2% MEKP was applied to a waxed glass surface and allowed to set for a specified period of time. A glass mat was applied to the tacky surface and the resin was rolled into it using a teflon roller to provide a resin rich layer. Three layers of woven roving were then applied with resin being rolled into each layer before the next one was added. The samples were cured to a constant barcol reading or for about 3 weeks before immersion in the test baths. Although certain experiments, testing the effects of lay-up variables, demanded departure from this procedure, the above procedure was used, unless otherwise stated.

When samples are placed in the water baths some delayed postcure may take place at the elevated water temperature. Much of the literature data available on composites was gathered on samples which were initially postcured at 90-100°C (200°F) for 1-4 hours. This is unfortunate since the materials tested are decidedly different from boat building materials which are cured at

Table 3.

Chemical Composition of Polyester Gel Coat and
Laminating Resins.

(Stars designate presence of constituent in material)

GEL COATS

MATERIAL SUPPLIER	IPA (NPG)	OPA (NPG)	VINYL
1	*		
2	*		
3		*	
4	*		
5			*
6	*		
7	*		
8	*		
9	*		

LAMINATING RESINS

MATERIAL SUPPLIER	IPA	OPA	NPG	EG	PG	TMPD
1	*		*	*		
2		*		*		
3		*			*	
4	*					*
5		*			*	

IPA - ISOPHTHALIC ACID
OPA - ORTHOPHTHALIC ACID
NPG - NEOPENTYL GLYCOL
EG - ETHYLENE GLYCOL

PG - PROPYLENE GLYCOL
VINYL - URETHANE BASED POLYESTER
RESIN
TMPD - 2,2,4 - TRIMETHYL - 1,3
PENTANE DIOL

FIBER GLASS REINFORCEMENT

1. 3/4 oz. Mat
2. 1 1/2 oz. Mat.
3. 24 oz. woven roving
4. 20% by weight chopped gun roving (1 1/2 oz. strand)
5. Nylon stitched fab mat.

ambient temperature. In our experiments, the samples were cured under ambient conditions. No elevated temperature postcures were made. Most samples were made and postcured at room temperature but a series of panels were made and postcured at 50, 75, 90 100°F to test the effects of manufacturing temperature.

Samples were tested for blister resistance by immersion in a 65°C (149°F) ± 0.2°C (2°F) circulating water bath which is shown in Figure 12. Some samples received two sided exposure by direct immersion in the bath while other samples were exposed only on the gel coat side. Figure 13 shows the acrylic sample holders which were designed for one sided exposure. These tanks have the specified advantage, over the one sided sample holders, that one set of samples can be removed and studied without interrupting the other tests that are in progress. Samples were removed, examined for blister initiation, blister size and extent of blistering, on a routine basis. Some samples were weighed to observe weight changes.

The data on sample construction, blister initiation time and blister severity are listed in Table 4. The construction of the panel is given in column 2. The numbers indicates gel coat resin, laminating resin, type glass used in resin rich area, type glass used in back-up laminate, respectively. For example 4-3-1-3 indicates a vinyl gel coat on a PG orthophthalic laminate made with a transition layer containing a 3/4 oz. mat and then 3 layers of 24 oz. woven roving.

A number of subsets of experiments were included in this research. This included procedures to determine the severity of blistering by counting the number of blisters per square centimeter using an oblique light to cast shadows and by estimating the fraction of the area that was covered. Data for a series of panels, with different combinations of resins, were followed for a



Figure 12. Isothermal baths used in the study of laminate-water interactions. These baths contain distilled water at 65°C.

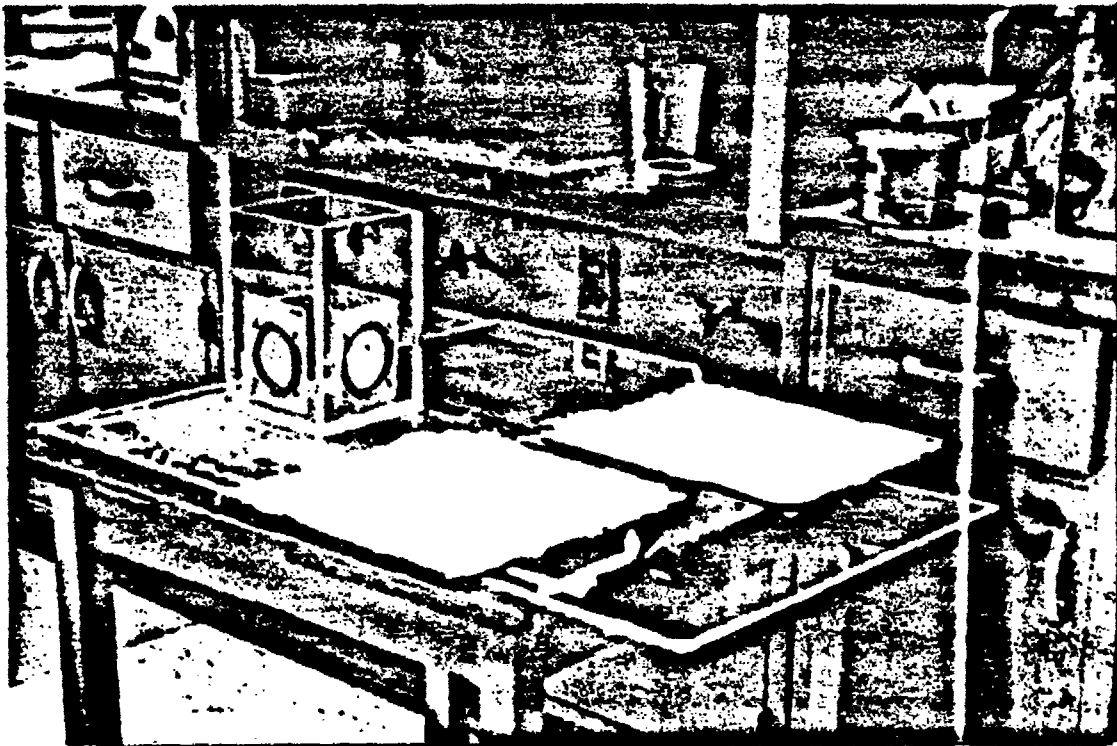


Figure 13. Acrylic test tank designed for single side exposure of the laminates with the 65°C distilled water. The white sheets represent laminates prepared using lab techniques.

Table 4

Experimental Results

Sample #	MAILS G-L-M-R	Fab. Temp. (°F)	Gel Coat Set Time (hrs.)	# of Sides Exposed	Blister Init. Time (< hrs.)	Immersion Time (hrs.)	Size of Blisters (cm ²)	% Surface Covered	Comments
ISO/CRHD EG									
3B	1-2-1-3	RT	0	2	500*	7031	0-.01	80	All samples-slight yellowing c gel coat surface
3C	"	"	"	2	500*	6887	0-.01	90	
3F	"	"	"	1	478*	4127	.02-.04	15	50°C Bath
3H	"	"	"	2	NB	692			
3I	"	"	"	2	216*	4222	-.01	90	
ISO/CRHD EG - Male Male									
7A	1-2-1-3	RT	-	2	NB	6406			All samples - print through & gray gray color
7B	"	"	-	2	NB	7031			
7C	"	"	-	2	NB	3384			Small
7E	"	"	-	2	720*	4222			
7F	"	"	-	2					
7G	"	"	-	2	NB	4007			
7H	"	"	-	1	NB	4007			
CRHD EG - No gel coat									
11A	-2-1-3	RT	-	2	NR	6862		Small	Blister & crack
11B	"	"	-	2	NR	6406			
11D	"	"	-	2	286*	286	.0-.21	5	Blisters disappeared Crack
11E	"	"	-	2	NR	6935			
11G	"	"	-	2					Small Blisters disappeared
11H	"	"	-	2	216*	4222		Small	
11I	"	"	-	2	120	4127		Small	Blisters disappeared
Resins only									
29A	1—	RT	-	2					
29B	-2—	RT	-	2					
ISO/CRHD EG									
32B	1-2-1-2	RT	1.0	2	216*	4222	.01-.6	95	Cracks up to 2mm
32F	"	"	"	2	48	552	.01-.06	20	
32G	"	"	"	2	48				
ISO/CRHD EG									
34A	1-2-1-3	RT	96.0	1	24	2568	.04-.8	40	One blister cracked
34B	"	"	"	1	360*	4007	.04-1.2	60	Crack length of sample
34C	"	"	"	2	72	4222	.08-1.0	80	
34E	"	"	"	2	NR				

Table 4 (continued)

ORHD/ORHD FG 37 mil (wet) gel coat

41A	3-3-1-3	RT	0.5	1	1464	2160	.02-1.0	10	All samples
41B	"	"	"	1		2500	0	0	Discoloration
41D	"	"	"	2		1400	0	0	"
41E	"	"	"	2					
41F	"	"	"	1	NR	2831	.3-.5	"	
41H	"	"	"	1		2831		"	
41J	"	"	"	1		744	0	0	"
41K	"	"	"	2		1400	0	0	

ISO/ORHD FG

64A	2-3-1-3	RT	1	2	480	2655	.04-.8	10	All samples
64B	"	"	"	2	249				discoloration
64C	"	"	"	2	264				
64D	"	"	"	1	NR	2376			
64E	"	"	"	1	456	2831	1.2-1.35	5	
64F	"	"	"	2	NB	692			50°C bath
64G	"	"	"	1	119	839	.01-1.3	20	
64H	"	"	"	1	35	1075	.01-.70	10	
64I	"	"	"	1	336	1056	3.0	15	1 very large blister

ORHD/ORHD FG

65B	3-3-1-3	RT	1	1	456	2831	.5-1.5	50	All samples
65E	"	"	"	1	384	2831	.3-1.5	40	discoloration
65F	"	"	"	2	582	3169	.16-1.35	20	
65K	"	"	"	2	408	1128	.1-.6	15	very shallow blisters
65O	"	"	"	2	336	1056	.1-.3	10	

ISO/ORHD FG

67B	1-3-1-3	RT	1	2	NR	NR	.05	40	
67G	"	"	"	2	NR	NR	.05-.3	20	
67I	"	"	"	2	336	3169	.09-.25	10	

ISO/ORHD FG - 25 mil (cured) gel coat

77A	2-3-1-3	RT	1	1	462	2831	1.0-1.5	25	
77B	"	"	"	2	480	1200	.01-.56	25	
77C	"	"	"	2	480	2855	.25-.5	10	
77D	"	"	"	1	456	2831	.2-.9	10	
77F	"	"	"	2	432	1152	.01-.2	10	
77J	"	"	"	2	NR	NR	1-1.8	40	
77G	"	"	"	1	NR	3169	.04-.8	20	

ISO/ISO(G) - Gel coat resin used throughout

87B	2-2-3	RT	1	2	288	1813	.02-.16	2	
87C	"	"	"	1	456	1056	≈0.5	1	
87F	"	"	"	1	NB	1056	0	0	
87G	"	"	"	2	500	NR	≈.04	5	

ISO/ISO

88A	2-1-1-3	RT	1	1	404*	1056	.04	1	Shallow blisters
88B	"	"	"	2	192	912	.01-.225	35	
88C	"	"	"	1	435*	1056	.02	1	
88D	2-1-1-3	RT	1	2	216	936	.01-.165	20	

Table 4 (continued)

CRHD/ISO	3-1-1-3	RT	48	2	44				
93D									
CRHD/ISO	3-1-1-3	RT	1	1	188	1536	-.1	10	
95A	"	"	"	1	168	1536	.02-.3	10	
95C	"	"	"	1	NR	1536	small	10	
95E	"	"	"	2	NR	500	small	10	
95F	"	"	"	1	212	1536	-.1	10	
95H	"	"	"	2	118	838	.02-.18	10	
95B	"	"	"	2	100	820	.01-.2	30	Thin rippled gel coat
95G	"	"	"						
CRHD/ISO	3-1-1-3	40x5	1	2	256	976	.04	10	Glass went into gel coat during layup
96A	"	"	"	2	18	500			
96C	"	"	"	1	331	1680	.02-.2	10	
96D	"	"	"	1	44	1680	.02-.2	10	
96E	"	"	"	1	44	1680	.02-.2	10	
96G	"	"	"	1	44	1680	.02-.2	10	
96I	"	"	"	1	44	1680	.02-.2	10	
ISO(w)/ISO	4-1-1-3	RT	1	1	164	355	.01-.02	3	
98A	"	"	"	1	355*	355	.01	2	
98B	"	"	"	2	164				
98C									
ISO(w)/CRHD FG	4-3-1-3	RT	1	1	190	910	.01-.6	30	
99C	"	"	"	1	190	910	.01-.5	20	
99D	"	"	"	1	190	910	.01-.18	10	
99F	"	"	"	1	290	1010	.01-.18	10	
99G									
ISO/CRHD FG	2-3-1-3	50x5	1	1	190	910	.01-.72	30	
116A	"	"	"	1	190	910	.01-1.06	30	
116B	"	"	"	1	290	1010	.01-.79	40	
116C	"	"	"	1	480	1200	.01-.54	20	
116D									
CRHD/CRHD FG	3-3-1-3	50x5	1						
117									
ISO/CRHD FG	2-3-1-3	90x2	1	1	190	910	.01-1.1	30	
123A	"	"	"	1	623	1343	.01-1.17	30	
123B	"	"	"	1	290	1010	.01-.76	30	
123C	"	"	"	1	480	1200	.01-1.36	40	
123D									
CRHD/CRHD FG	3-3-1-3	90x2	1						
127									
VINYL/CRHD FG	5-3-1-3	RT	1	2	148	868	.01-.3	30	
128B	"	"	"	2	214	934	.01-.24	10	
128H									

Table 4 (continued)

VINYL/CHLORO PG									
3-38B	5-1-1-3	RT	1	2	124	844	.01-.25	10	
3-38C	"	"	"	2	100	820	.01-.3	20	
ISO/CHLORO PG									
3-43A	2-3-1-3	100+2	1	1	408	1128	.01-.11	35	
3-43B	"	"	"	1	408	1128	.01-.10	40	
3-43C	"	"	"	1	288	1008	.01-.15	20	
3-43E	"	"	"	1	288	1008	.01-.12	40	
ISO/CHLORO PG									
1-57A	6-5-(1-4-4)- (2-3)	RT	0.50	1	118/600	938	.1-1.4	90	Surface/gel coat
1-57B	6-5-(4-4)- (2-3)	RT	"	1	118/336	938	.1-.8	70	Surface/gel coat
1-57C	6-5-(1-2-2)- (2-3)	RT	"	1	118/168	938	0-.15	70	Surface/gel coat
1-57D	6-5-(2-2)- (2-3)	RT	"	1	91/938	2640	.1-2	25	Surface/gel coat
ISO/CHLORO PG									
0-A	7-(6/4)-5	RT	NA	2	168	1680/15mo	.5-1/<.5	>.5 cracks/>.5 cracks	
B	7-(7/4)-5	RT	"	2	168	"	<.5/.5-1	<.5 cracks/>.5 cracks	
C	7-4--5	RT	"	2	168	"	<.5-1/<.5	>.5 cracks/>.5 cracks	
D	9-(7/4)-5	RT	"	2	168	"	<.5/<.5		
E	8-4--5	RT	"	2	168	"	<.5/<.5		
F	8-(6/4)-5	RT	"	2	168	"	<.5/<.5		
G	9-(6/4)-5	RT	"	2	168	"	<.5/<.5	>.5 cracks/>.5 cracks	
I	8-(7/4)-5	RT	"	2	168	"	.5-1/<.5		
J	7-(8-4)-5	RT	"	2	168	"	<.5/<.5	<.5 cracks/>.5 cracks	

Footnotes: RT = Room temperature, * indicates accurate within 150 hrs., NR = Blister initiation time not recorded,
NB = no blisters observed

1 month. These samples received two sided exposure by direct immersion in the bath. Another set involving layup and post curing at different temperatures received 1 sided exposure using the sample holders. The blister initiation time and severity at one month for both of these sets are given in Table 5.

Series 1-57 panels were made using a spray gun. construction and results are listed in Table 4. A variety of designs were used for the resin rich layers between the gel coat and the laminate. For instance, the resin rich layer of sample 1-57a had 1 layer of 3/4 oz. mat, then 2 layers containing 20% chopped gun roving. This was backed with three alternate layers of 1 1/2 oz. mat and 24 oz. roving.

Series 0, which primarily tested gel coats from three different suppliers, also was laid-up using spray guns and had a 1/2 mil colored marker layer of gel coat resin between the gel coat and the laminate. No other resin rich layer was used. Nylon stitched fab mat. was used in the laminate layers. The resins were BPO promoted. The laminate construction and the results are listed in Table 4.

Net Weight Change Experiments

The change in weight was determined for selected samples on a routine basis. These samples were removed from the bath, dried, and weighted to the nearest 0.0001 grams on a electronic balance. The samples, then, were returned to the bath. The results are given in Table 6. Variations in weight loss for selected samples are plotted in Figures 14-20.

Table 5

**Blister Severity Data for Selected Samples
(30 days after Blister Initiation)**

Test	Resins	Blister Initiation	Maximum Blister	Blister Density	Surface Covered		
Laminate	(GEL/LAM)	Time (Hrs.)	Size (Cm ²)	(Blisters/Cm ²)	(%)	$\frac{\text{Density} \times \text{Size}}{2} \times 100$	
88	B	ISO/ISO (19 mil)	192*	0.23	5.20	35	60
	D		216*	0.17	2.80	20	23
95	B	ORTHO/ISO	118*	0.18	3.24	10	29
	G		100*	0.20	7.12	30	70
3-39	B	Vinyl/ISO	124*	0.25	3.68	10	46
	C		100*	0.30	4.88	20	73
128	B	Vinyl/ORTHO	148*	0.32	3.36	30	54
	H		214*	0.24	0.32	10	3.8
65	K	ORTHO/ORTHO	408*	0.60	1.92	15	58
	O		336*	0.30	1.84	10	28
77	B	ISO/ORTHO (25 mil)	480*	0.54	1.44	25	39
	F		432*	0.20	3.20	10	32
64	G	ISO/ORTHO	119	1.3	1.2	20	78
	H		355	0.7	1.0	10	35
	B		249*	-	-	-	-
	C		264*	-	-	-	-
116	B	ISO/ORTHO (500F)	190	1.08	1.2	30	65
	C		290	0.79	2.72	40	107
	D		480	0.54	1.12	20	30
	A		190	0.72	-	30	43
123	A	ISO/ORTHO (900F)	190	1.1	1.28	30	70
	B		623	1.17	1.28	30	75
	C		290	0.76	1.84	30	70
	D		480	1.32	1.36	40	90
3-43	A	ISO/ORTHO (1000F)	408	0.11	6.1	35	34
	B		408	0.10	7.2	40	36
	C		288	0.15	3.76	20	28
	E		288	0.12	6.0	40	36

* 2 side exposure

Table 6

Net Weight Change Data

Sample #	Blister Initiation Time (< hrs.)	Max. Wt. Time (hrs.)	Max. Wt. Increase (%)	# Sides Exposed	Comments
3 ISO/ORTHO EG					
B	500*	400-600	1.82	2	
C	500*	649	1.89	2	
I	216*	715	2.5	2	
7 ISO/ORTHO EG Male Mold					
A		524	2.31	2	
B		550	2.56	2	
C	720*	528 (1032)	2.3(2.31)	2	
E		714	2.47	2	
11 ORTHO EG No Gel Coat					
B		548	2.07	2	
E		602	2.34	2	
H	216*	715	2.3	2	
I	120			2	
29 Resin					
A (NPG ISO)		5778	2.1	2	
B (ORTHO EG)		910	6.78	2	
32 ISO/ORTHO EG					
B	216*	2498	4.1	2	Cracks
F	48				
G	48				
34 ISO/ORTHO EG					
C	72	1389-2902	3.46	2	
A	24				
43 Gel Coat					
A ISO NPG		574	7.6	2	
B ORTHO NPG		574	15.45	2	
C ISO (unfilled)		574	6.4	2	
64 ISO/ORTHO PG					
D		1273	1.9	1	
65 ORTHO/ORTHO PG					
F	582*	2711	2.2	2	
67 ISO/ORTHO PG (25 mil cured gel coat)					
F		718(>1273)	1.79(1.7)	2	
I	336				

Table 6 (continued)

77 ISO/ORTHO PG				
J		1870	1.5	2
E	452			
96 ISO/ORTHO PG (400F lay up)				
D	331*	140	0.02	1
E	44	140	0.05	1
G	44	140	0.06	1
I	44	140	0.006	1
95 ORTHO/ISO				
A	188	312	0.48	1
C	168	312	0.51	1
E		312	0.50	1
H	212	312	0.52	1
99 ISO/ORTHO				
C	190	>1000	0.15	1
D	190	>1000	0.12	1
F	190	>1000	0.17	1
G	190	> 100	0.18	1
116 ISO/ORTHO PG (500F lay up)				
A	190	>1000	>0.15	1
B	190	>1000	>0.27	1
C	290	>1000	>0.19	1
D	480	>1000	>0.29	1
123 ISO/ORTHO PG (900F lay up)				
A	190	>1000	>0.39	1
B	623	>1000	>0.42	1
C	290	>1000	>0.38	1
D	480	>1000	>0.32	1
ORTHO Resin in different solvents at room temperature				
Water		588	8.9	2
0.05M glycol		300	7.1	2
0.05M phthalic acid		300	8.56	2

SAMPLE 29A

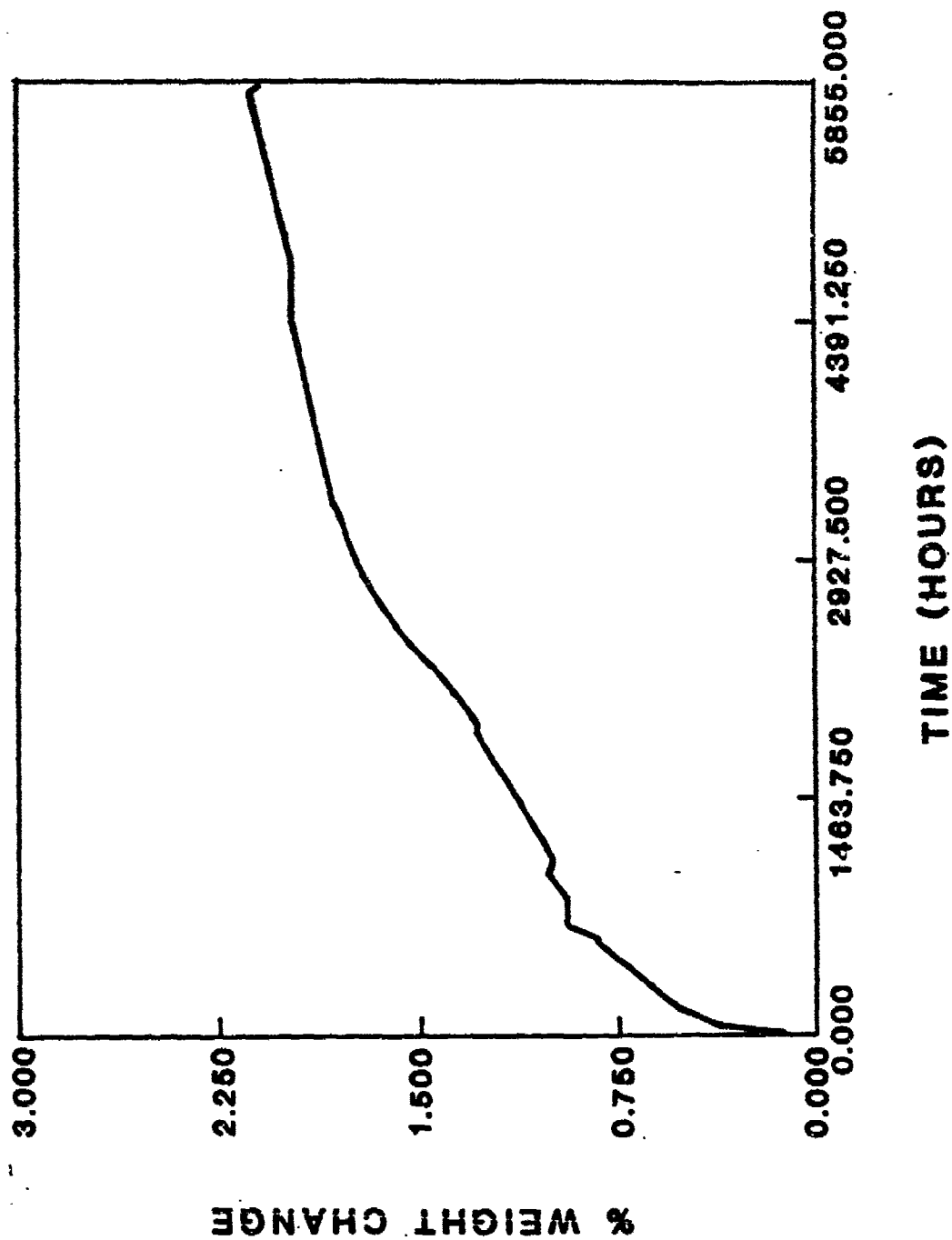


Figure 14. Effect of immersion time on weight of gel coat.

GEL COATS

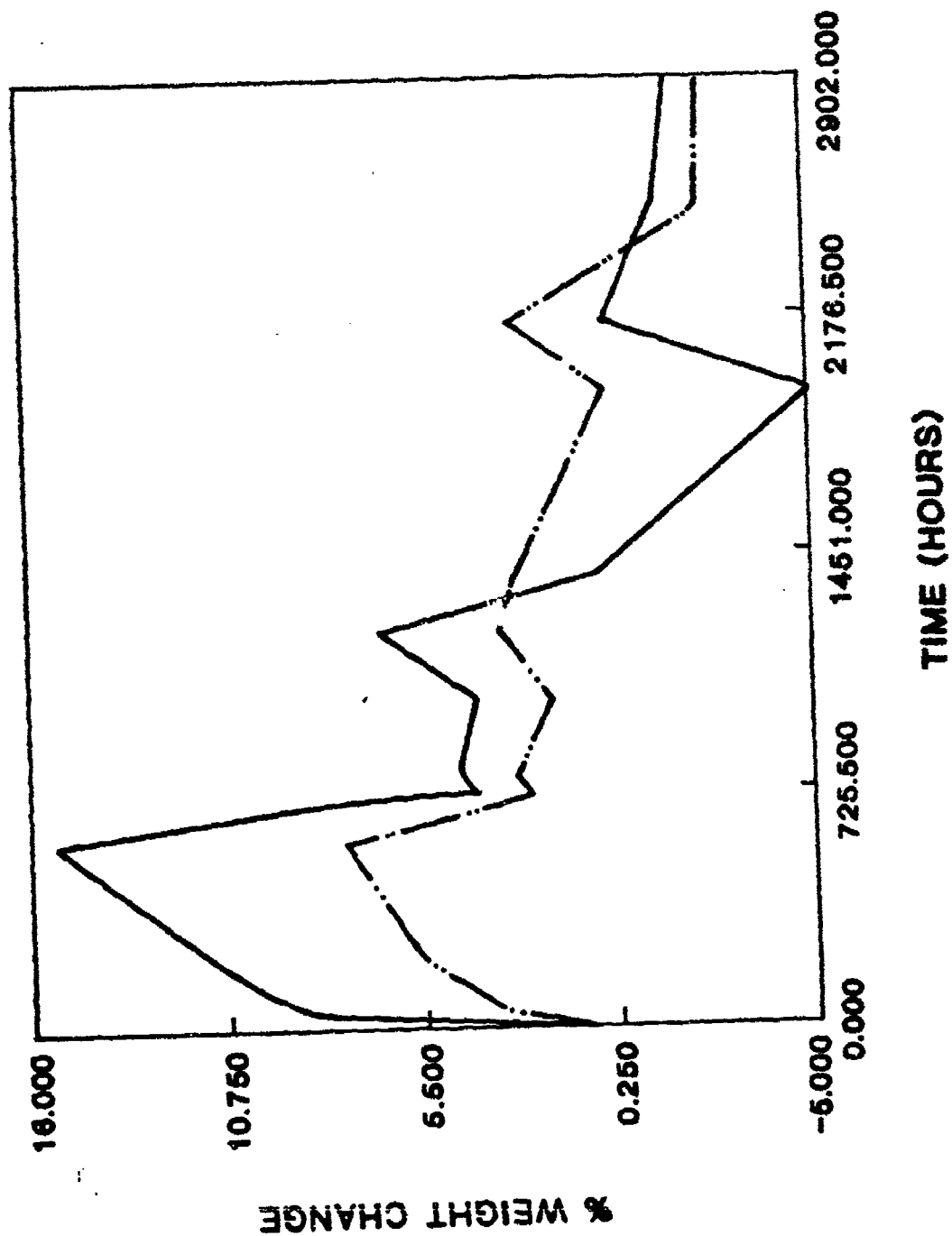


Figure 15. Effect of immersion time on weight of gel coats.

GEL COATS

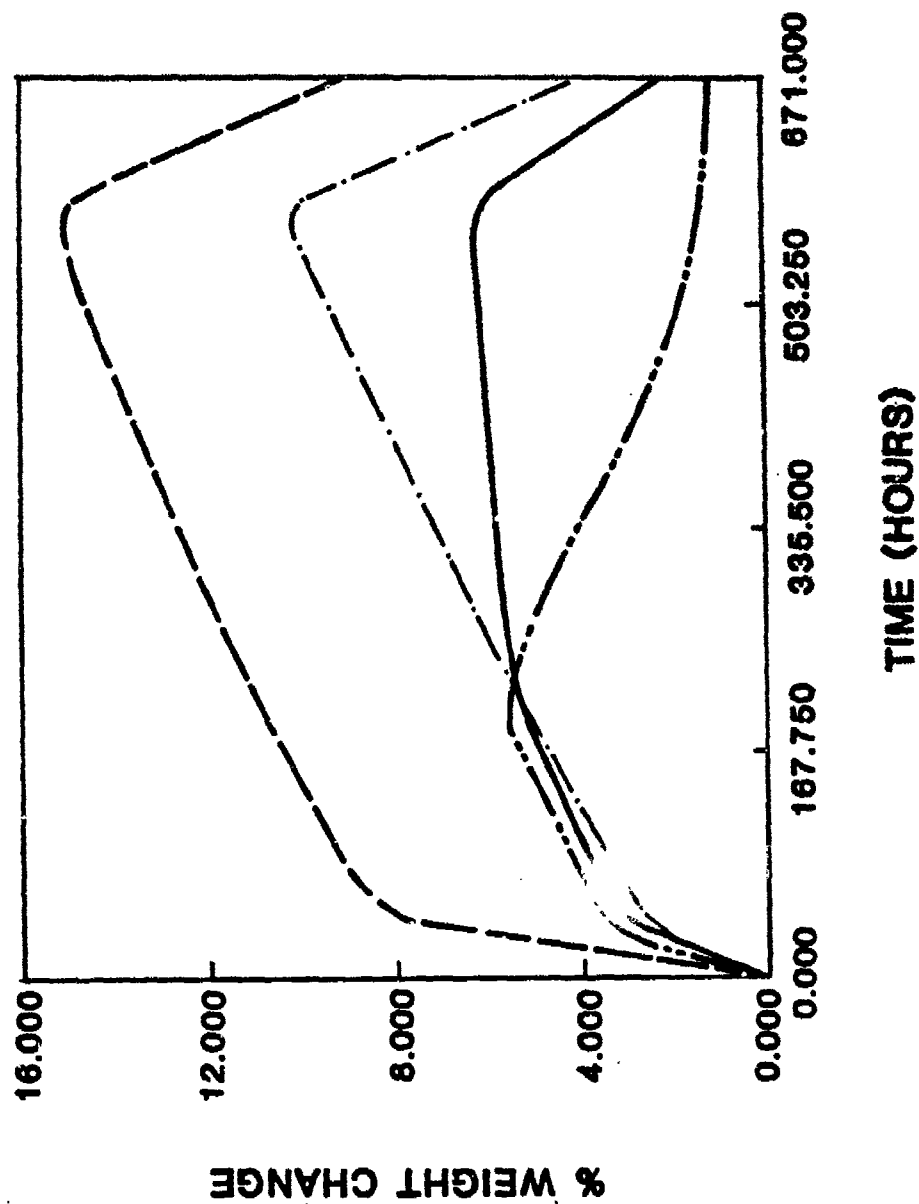


Figure 16. Effect of immersion time on weight of gel coats.

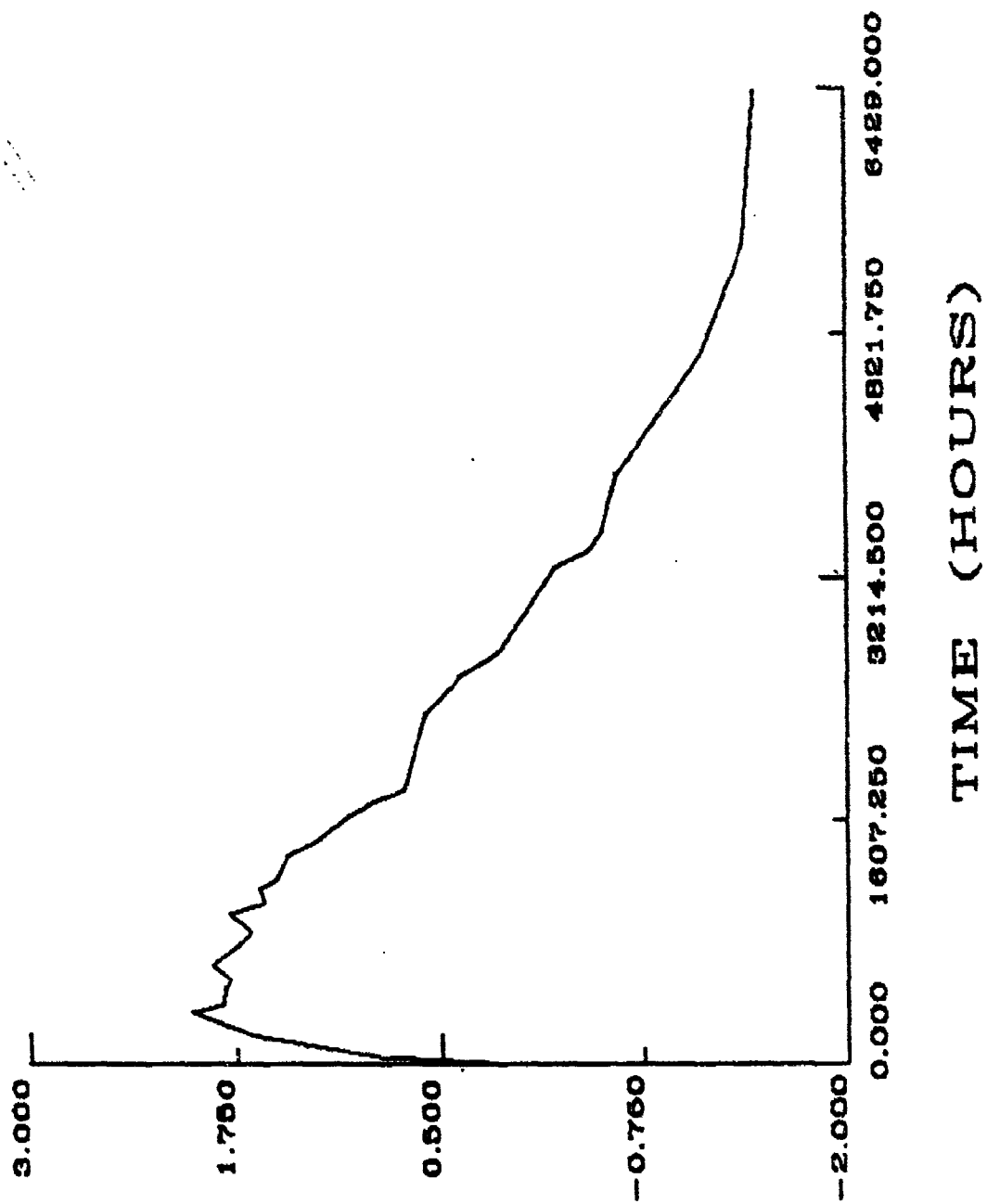


Figure 17 Percent weight gain for sample 3C.

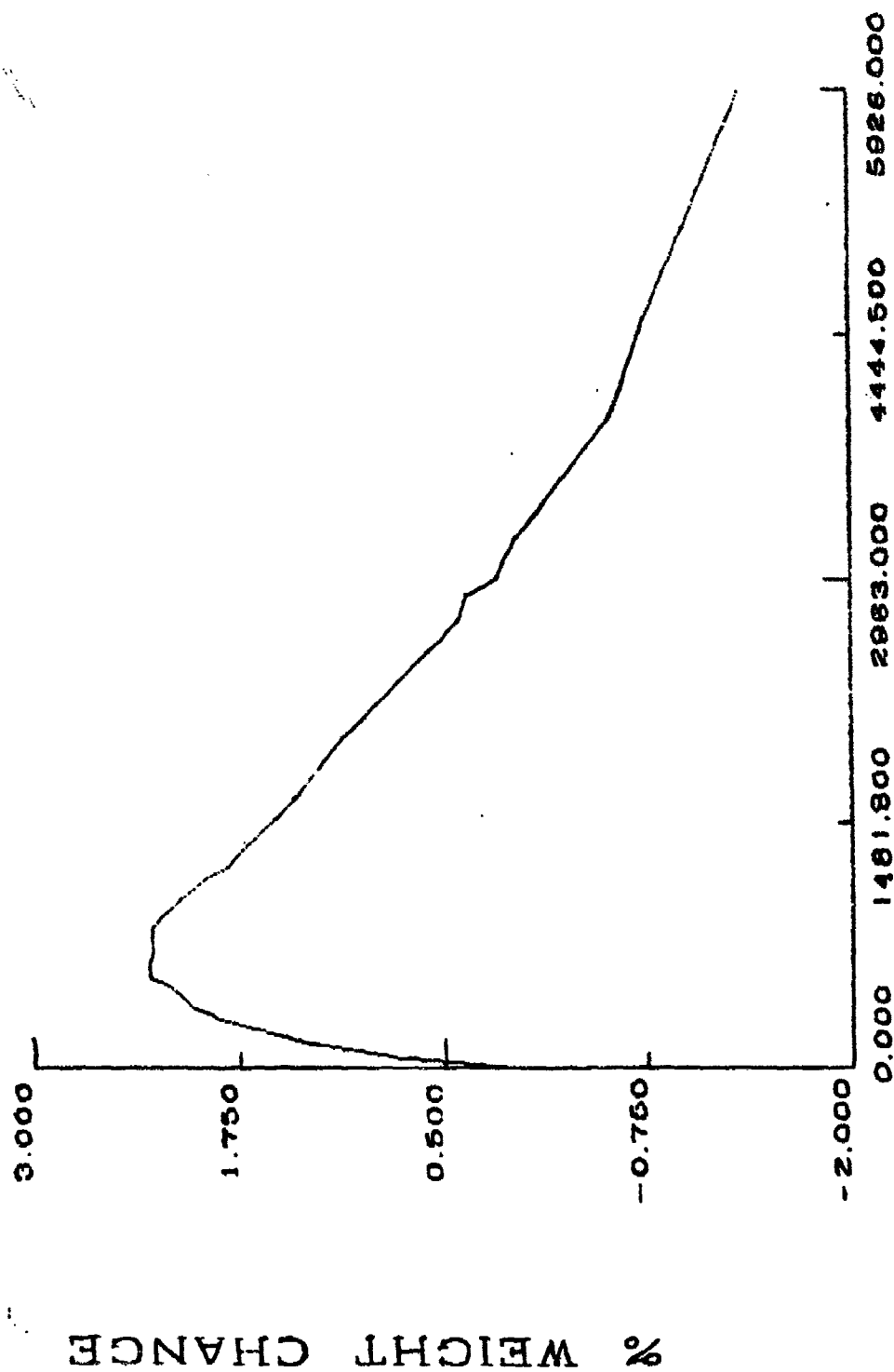


Figure 18 Percent weight gain for sample 7A.

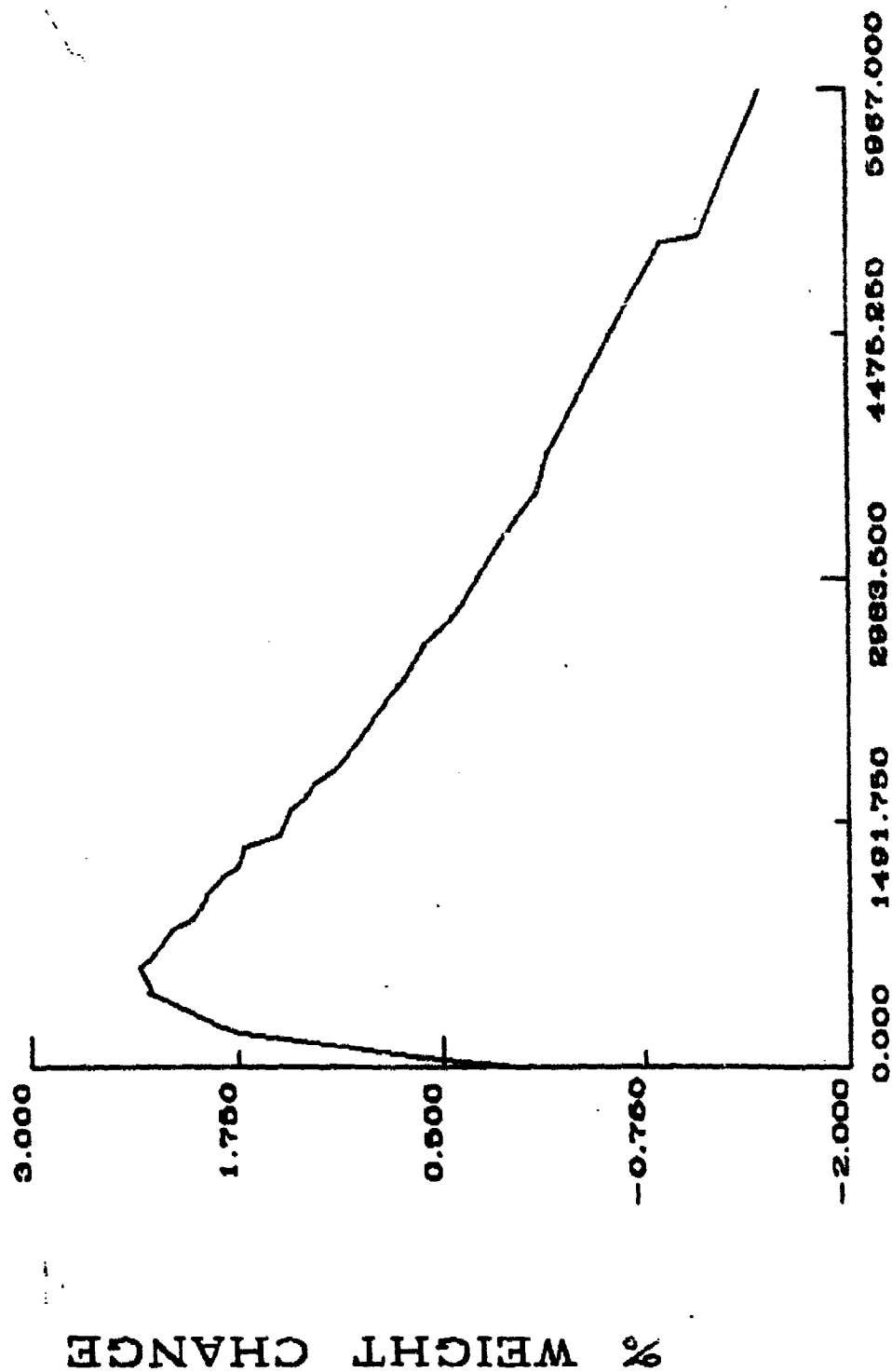


Figure 19 Percent weight gain for sample 11E.

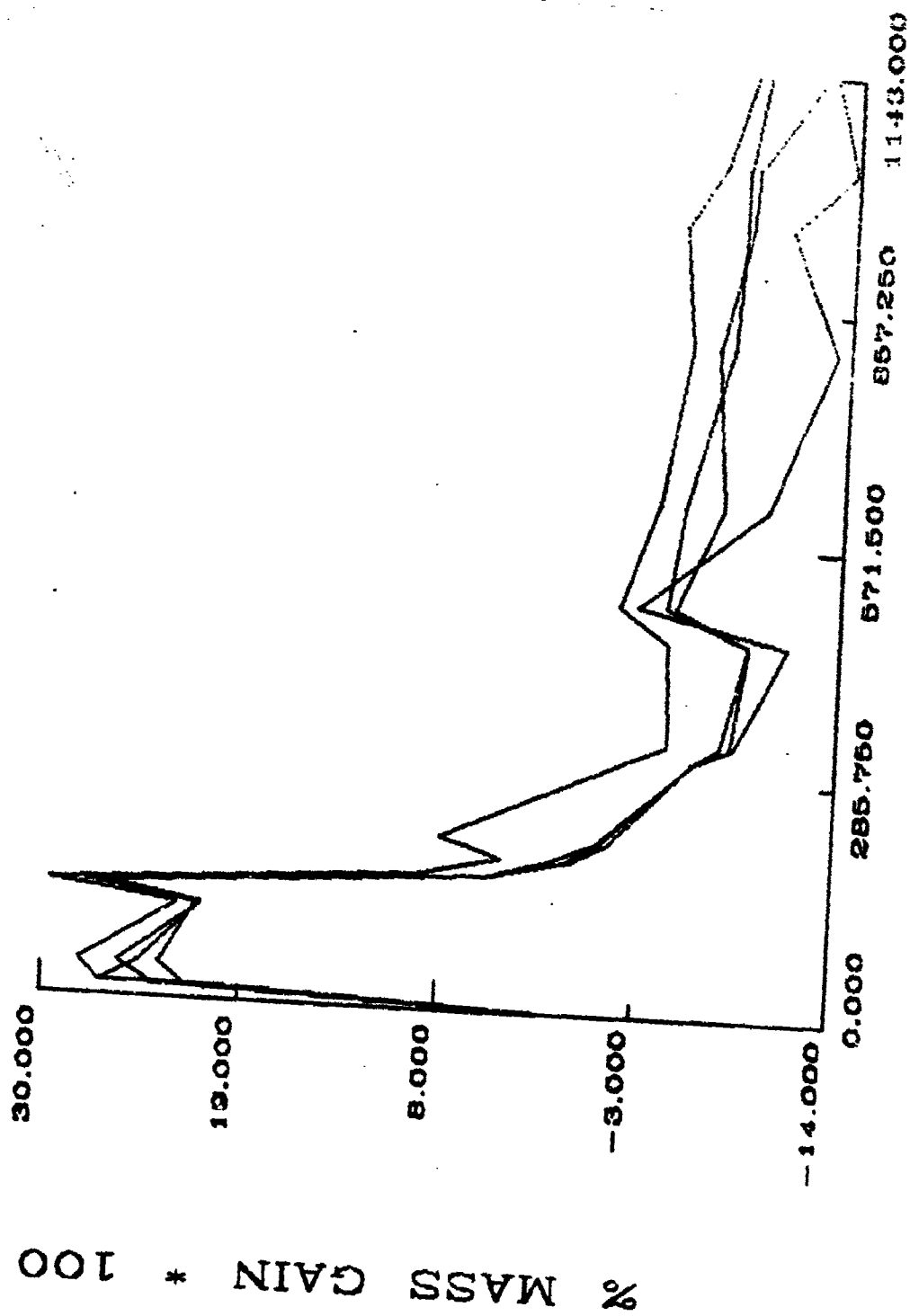


Figure 20 Percent weight gain for 96 Series.

Permeability Studies

The rate at which water is transferred through an isophthalic gel-coat was determined as follows. A thin section of gel coat was placed into a diffusion apparatus which allows water to diffuse through the section. One surface of the gel coat was in constant contact with the distilled water, while the opposite surface was exposed to surrounding conditions. To obtain a knowledge on the largest possible permeation rate, this apparatus was placed in a dessicator containing calcium chloride. This environment is virtually water free, allowing for very little resistance to mass transfer within the air (i.e. resistance to water movement within the gel coat is controlling).

The following data was used in the calculation of the water permeation rate.

1. Exposed surface area 11.4 cm²
2. Thickness 0.07 cm (28 mils)
3. Mass and time data for the sample

A rate of 1.087×10^{-4} g H₂O/hr was determined as the steady state value of permeation for an NPG isophthalic gel coat resin. Steady state water permeation was obtained in approximately 300 hours. From this permeation rate a flux of water (J) was determined to be 9.535×10^{-6} g H₂O/cm²/hr, which corresponds to a normalized flux (Jx thickness/1cm) of 6.6745×10^{-7} gm H₂Oxcm/cm².hr.

As expressed earlier, this is the largest flux attainable through this particular gel coat (ISO-NPG). An interesting observation can be seen from these results. It would take roughly three months to pass one cup of water through a 1 square foot section of a 20 mil ISO-NPG gel coat.

Exotherm Experiment

The purpose of these experiments was to observe the temperature change during the polymerization (crosslinking) reaction of MEKP catalyzed polyester-resin.

The free radical reaction causes the conversion of double bonds to cross-linked single bonds. The chemical reactions give off heat (exotherm) which is related to the number of crosslinked sites. We expected to observe large temperature increases in the peroxide initiated polyester resin systems, as suggested both in the literature (22) and in reports from people in the industry.

We performed several tests curing with 2% MEKP at ambient temperatures. Thermocouples were used to measure the temperature changes within the curing laminate. the result are given in Table 7 and plotted in Figure 21.

Air Inhibition Studies

A series of panels were constructed in the normal manner with the primary variable being the time between the layup of the gel coat and the laminating resin. In this manner, the time the inner surface of the gel coat was exposed to air was varied. A set of panels also were constructed using a male mold technique so that the gel coat was applied immediately after the laminate. The outer surface of the gel coat was then exposed to air during the full cure. Another set was made without a gel coat. In addition, samples of gel coat and laminating resins were cast on a waxed glass plate and allowed to cure with one side against the mold and the other side exposed to air. After these samples were cured they were immersed in the 65°C water bath and observed in the same manner as the other samples. The results are given in Table 4 and 6 (see series - 3, 32 and 34 for the EG orthophthalic laminating resin with a

Table 7

Peak Exotherm Temperature

RESIN TYPE		INITIAL	GEL TIME	PEAK EXOTHERM
Laminating Resin - LR		TEMPERATURE	OR KICK-OFF	TEMPERATURE
Gel Coat - GC		(+ 20°F)	TIME (MIN)	(+ 20°F)
ORTHO - LR	3	40	19	88
ORTHO - LR	3	90	22	148
ORTHO - LR	3	75	2	146
ISO - LR	1	75	2	169
ORTHO - GC	3	75	2	116

EXOTHERMS

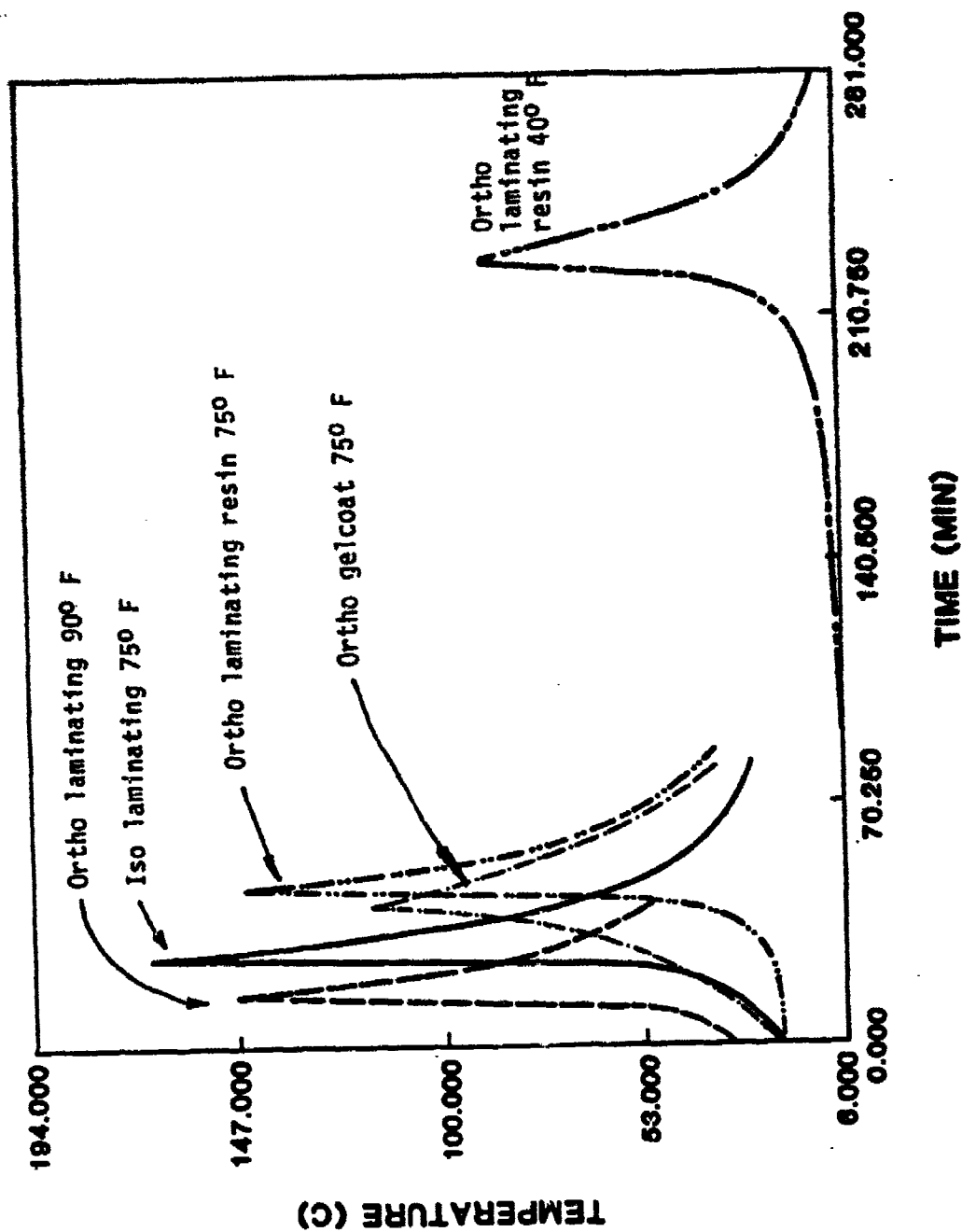


Figure 21 Exotherm results.

NPG isophthalic gel coat, series 64, 67, 77 for NPG isophthalic gel coated PG orthophthalic laminates, series 65 and 93 for NPG orthophthalic gel coated on the NPG/EG isophthalic laminating resin, series 7 for the male mold construction, series 11 for the samples with no gel coat and series 29 and 43 for the resins).

Microscopic Studies

In order to get a better understanding of the structure of blisters, blisters were cross sectioned using a thin sectioning technique. This allowed the blistering process to be investigated on a microscopic level with the use of a polarizing light microscope. The sections not only showed the internal structure of the polyester composite, but also showed the location, and the growth process of the blister. This permitted us to explore the cause and effect relationships associated with blistering in fiberglass reinforced polyester resins.

After a blister was isolated, the blister to be cross-sectioned was cut out of the composite with a key saw. The sample was then sliced into thin sections by the use of a diamond saw, with water as a coolant. The thin diamond blade allowed the preservation of most of the blister. This gave a series of sections, one following the other, as in a motion picture. After the sectioning, the surfaces of the sections were ultrasonically cleaned in a methanol-water solution polished with a series of abrasives and prepared on slides for microscopic viewing. The section was placed on the glass slide and imbedded in immersion oil. After a cover slide was put in place and the bubbles forced out, the slice was viewed.

High resolution photographs were taken of these sections and the sequence of blistering was determined. Although the saw does damage some of the

structure, most remain intact permitting a better understanding of blistering to be achieved (see Figure 10).

Blisters were seen to have initiated as a result of discontinuities in the polyester composite. Examples of these discontinuities observed are foreign particles (saw dust), air bubbles, disk cracks and low molecular weight fractions concentrated at the disk cracks. Certain slides indicate that osmotic cracks are another possible site for blister initiation. Figure 6 shows disk cracks surrounded by certain low molecular weight fractions, specifically cobalt salts, originating from unreacted promoter. These low molecular weight fractions can be seen as a halo around the disk crack. Once the disk crack forms a vacuum is created. The low molecular weight materials in the vicinity of the crack are drawn into this site, increasing the possibility of an osmotic solution forming.

A series of thin layers were observed in the laminates. These layers were 2-5 mils in thickness and occurred at surfaces which had cured for a period of time before the next layer was added. these layers exhibited birefringence under the polarizing microscope. It is assumed that these are styrene rich layers but further experiments are needed to determine the sources and composition of these layers.

Stress Measurement Experiments

The microscopic examinations described above clearly show that internal cracks form in the composite material. While some of the late cracking is due to osmotic pressure, there is clearly some cracking due to stress buildup which takes place before the osmotic processes begin. Several experiments have been conducted to learn more about these stresses. In the first section of this report the stress fields that can be generated by the swelling caused

by water diffusion into the resin were discussed. Much of that discussion is theoretical and additional data must be collected to prove this hypothesis.

Internal cracks must be the result of internal stresses. The position of the internal stresses and the relative strength of the stress can be determined by two methods, polarized light and strain gauges. Stress fields cause birefringence in polymers which is visible when a polyester is viewed under polarized light, using crossed nicol prisms. This technique was used to examine stresses in polymers. However, to make quantitative measurements of the stress levels, an optical compensator lens is needed. Even then, it is impossible to separate the stress developed by water diffusion from the stress generated by the polymerization shrinkage during curing. Instead of pursuing this approach, a preliminary experiment were conducted using strain gauges. These gauges were embedded in the polymer, directly after the gel coat, as the laminate was built up. After polymerization, the stresses were measured and the strain gauges were zeroed. The material was then exposed to water and stress development was monitored. The results indicated that the stresses that develop in the laminate can be measured in this manner. However the technique must be refined to permit useful interpretation of the readings.

Trace Metal Analysis

One source of water soluble material is the inorganic cations in the resin additives. In order to evaluate potential sources of these ions, a series of resins were analyzed by x-ray fluorescent analysis. The data for a number of gel coat resins and one laminating resin are shown in Table 8.

Table 8

Qualitative X-Ray Fluorescent Analysis of Typical Polyester Resins and Gel Coat Materials.

ELEMENT	ISOPHTHALIC (NEOPENTYL GLYCOL)		ORTHOPHTHALIC (NEOPENTYL GLYCOL)	ORTHOPHTHALIC (PROPYLENE GLYCOL)	VINYL	POSSIBLE SOURCES
	GEL COAT A	GEL COAT B	GEL COAT	RESIN	GEL COAT	
Al	MODERATE	MODERATE	MODERATE	NONE	MODERATE	FILLERS (CLAYS) or FLAME RETARDANTS
As	TRACE	TRACE	TRACE	NONE	NONE	FILLERS (CLAYS)
Br	TRACE	TRACE	NONE	NONE	NONE	FILLERS (CLAYS)
Ca	HIGH	MODERATE	HIGH	LOW	NONE	FILLERS (CaCO ₃ or CLAYS)
Co	LOW	LOW	LOW	HIGH	NONE	PROMOTER
Cu	LOW	LOW	LOW	TRACE	NONE	PROMOTER
Fe	MODERATE	HIGH	MODERATE	LOW	HIGH	FILLERS (CLAYS)
K	LOW	NONE	LOW	NONE	MODERATE	FILLERS (CLAYS)
Mg	MODERATE	HIGH	HIGH	NONE	MODERATE	FILLERS (MgCO ₃ or CLAY
Mn	LOW	NONE	LOW	NONE	LOW	FILLERS (CLAYS)
Pb	TRACE	TRACE	NONE	NONE	NONE	FILLERS (CLAYS)
S	MODERATE	LOW	LOW	NONE	LOW	RESIN
Si	HIGH	HIGH	HIGH	HIGH	HIGH	THIXOTROPE AND CLAYS
Sr	LOW	LOW	LOW	NONE	NONE	FILLERS (CLAYS)
Ti	HIGH	HIGH	HIGH	LOW	HIGH	PIGMENT

III. DISCUSSION

A number of experiments were conducted to determine the factors that influence blistering. As more insight was obtained additional or new samples were run. In general the test panels fall into 6 categories. These include several series to determine the effect of: changing supplies, using various combinations of commercially available gel coats and laminating resins, the ambient temperature during construction and postcure, the types and amount of glass in the resin rich layer between the gel coat and the laminate, air inhibition of gel coat surface, and the rate of water uptake and leaching of resins and laminates.

Analysis of the results has led to a set of general conclusions which are presented and discussed below. Blister initiation time is a function of gel coat thickness as predicted by Fick's law of diffusion which was discussed earlier and confirmed by blister initiation studies by Crump (10) and by experiments 41 and 65 and experiments 64 and 77, in this study. As indicated earlier in this report, blisters do not form until water reaches the laminate layer and dissolves some water soluble material. The thicker the gel coat, the longer it takes for sufficient water to permeate to the initiation site. Thus comparison of blister initiation times for different samples are meaningless unless the gel coat thicknesses is the same or the blister initiation time is normalized to eliminate gel coat thickness differences.

Blister initiation times for a series of samples, is given in Table 9 and shown in Figure 22. The data indicate the effects of both thickness and resin selection. This data, normalized to a 14 mil gel coat thickness is shown in Figure 23. The data was adjusted by either calculating a rate per mil of gel coat thickness or by interpolation, if data were available for a

Table 9

**Blister Initiation Time for Selected Gel Coat-Resin
Combinations**

Test Laminate	Resin Combo (GEL/LAM)	Average Gel Coat Thickness (mils)	Average Blister Initiation Samples	Time (hrs.) Adjusted 14 mil
88 B, D	ISO/ISO	18.75	204	152
0 A-J	ISO/ISO	16	168	147
3-39 B,C	VINYL/ISO	12.9	112	122
95 B, G	ORTHO/ISO	14	109	109
65 K,U	ORTHO/ORTHO	14.25	372	366
64 B,C	ISO/ORTHO	13.10	257	272*
77 B,F	ISO/ORTHO	24.75	456	272*
128 B,H	VINYL/ORTHO	14.25	181	178

* by interpolation

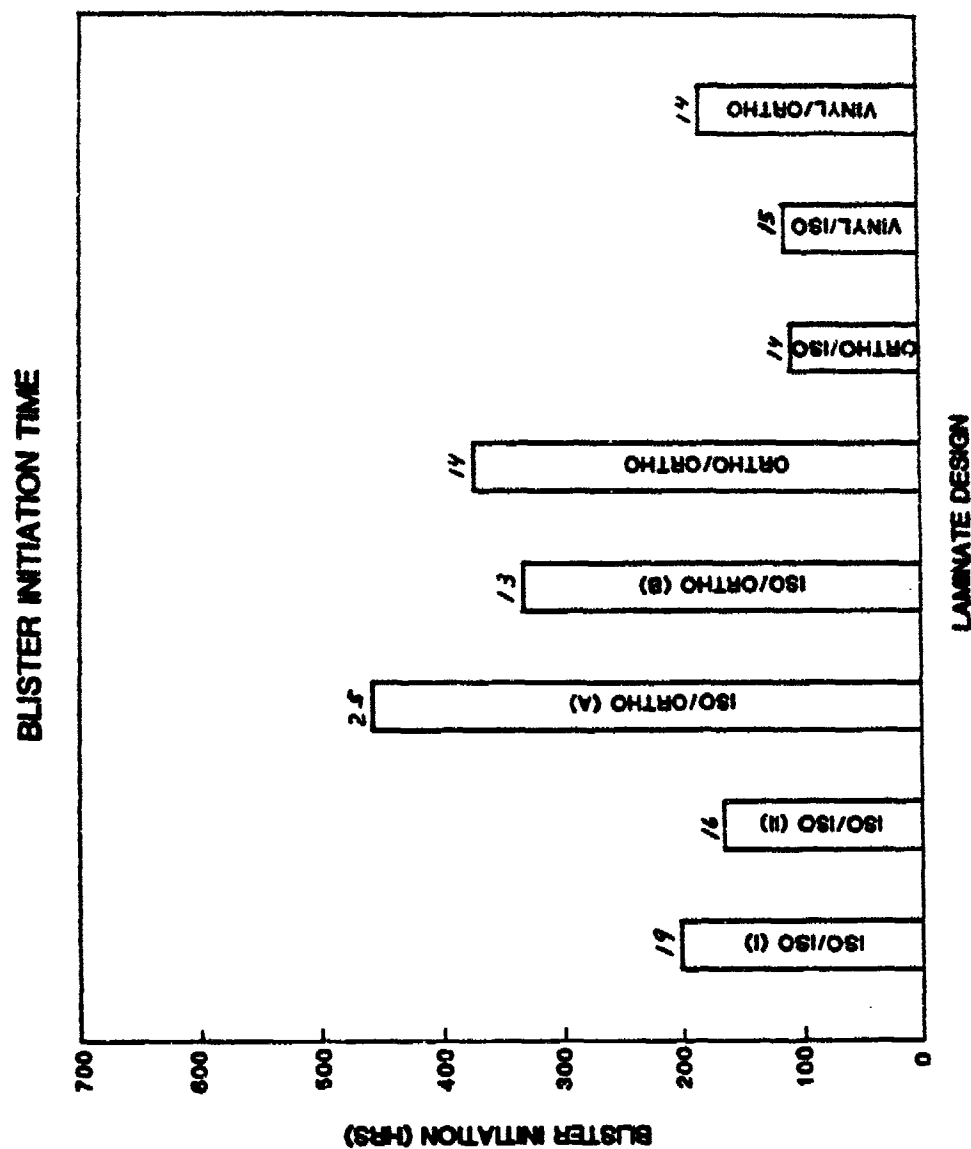


Figure 22 Blister initiation versus resin combination.

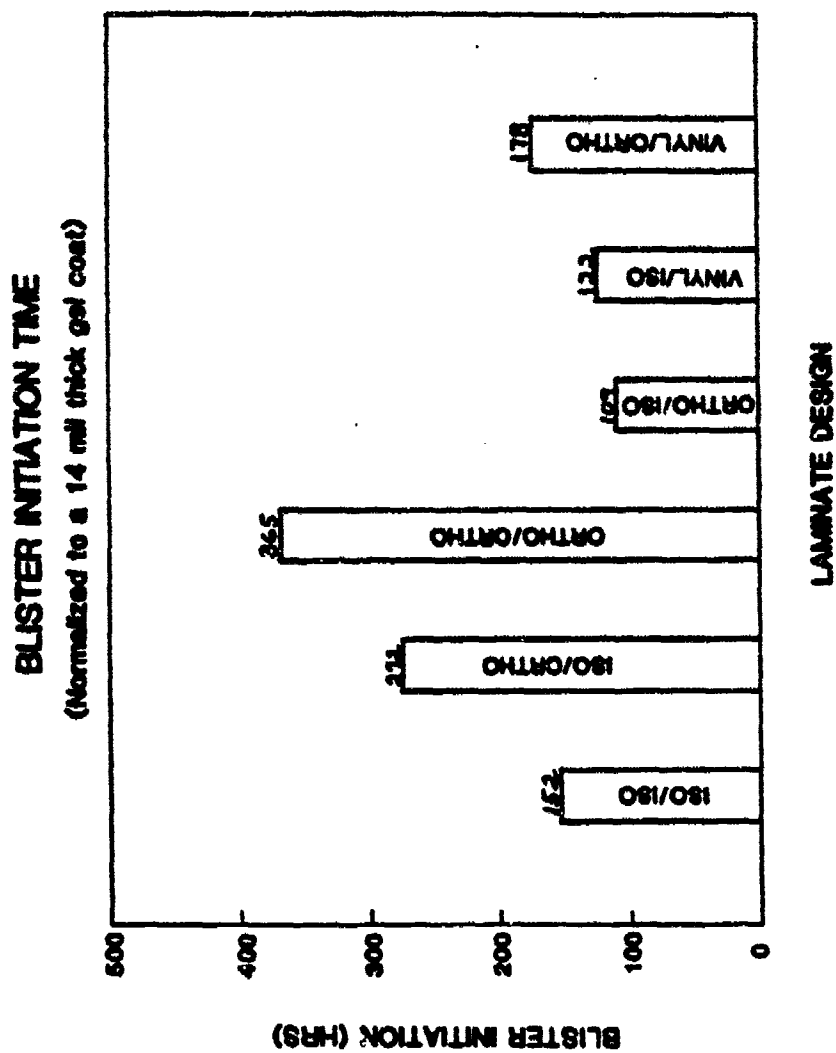


Figure 23 Blister initiation versus resin combination.
All gel coat thicknesses have been normalized
to 14 mils.

composite with two different thicknesses of the same gel coat. These data indicate that blister initiation time is a function of both the laminating resin and the gel coat formulation. In all cases samples made with PG orthophthalic laminating resins were better than those made with NPG/EG isophthalic resins. Results from initial experiments indicated that both of these resins produced laminates that were far superior to those made with EG orthophthalic laminating resin. On a PG orthophthalic laminating resin, the NPG orthophthalic gel coat was better than the NPG isophthalic gel coat which was better than the vinyl gel coat. The order changed when the same gel coats were used on NPG/EG isophthalic laminating resins with NPG isophthalic best, vinyl intermediate and NPG orthophthalic gel coat blistering the most quickly. It appears from our calculations and from our observations of birefringence, using a polarized microscope, that residual stresses created during layup and stresses produced by water related swelling account for some of these differences.

The severity of blistering 30 days after blister initiation, as measured by the density and size of the blisters, is a function of the laminating resin. The PG-orthophthalic resin resulted in fewer but larger blisters while the NPG-EG isophthalic resin produced more but smaller blisters, when NPG orthophthalic and NPG isophthalic gel coats were used. In both cases the total area affected was about the same. When vinyl gel coats were used both laminates produced approximately the same number of small blisters per square centimeter within the 30 day period. However, later examination of the samples indicate that the blisters on the sample with orthophthalic laminating resin increased in size and resembled those on the other orthophthalic samples. This delay may be due to the lower permeation rate for the vinyl gel coat. Samples made with NPG isophthalic gel coat on an EG orthophthalic laminating

resins, blistered more severely than isophthalic gel coated panels made with the other laminating resins. These samples developed cracks in the gel coat. In addition, the blister initiation time was not an indicator of blister severity. Samples which blistered early, may or may not develop a severe case of blisters. As indicated in Table 5 there was considerable variation in blister size and number within the sets.

The blister initiation time was approximately the same for similar gel coat materials regardless of supplier. However, the severity of blistering varied greatly among similar gel coats from different suppliers. In addition to blistering, some samples developed crazing. One reason for this could be the variations in filler and extender contents in the different gel coats made from the same base resin. Wide variation in metal ion content, as determined by x-ray fluorescence analysis, was noted in commercially available resins from different suppliers. As should be expected variations also were noted between gel coat and laminating resins. These differences, along with possible sources of each ion, are shown in Table 8.

The series of experiments made to test the effects of laminating a postcure temperature showed that lay-up temperatures between 50 and 90°F did not have a major influence on blister resistance for NPG-isophthalic gel coated orthophthalic laminates. However, these laminates did show an effect of temperature at 100°F. The high temperature laminates showed a higher density of blisters than the other laminates but the blisters were very small (less than 0.4 mm² surface area). At the low temperature, an NPG orthophthalic gel coat did not fully cure even after 100 hours. Although no significant difference could be found in the blister initiation time for these laminates, there was considerable variation between individual samples.

In the experiments with a resin rich backup layer, samples made with a chopped gun roving in this layer severely blistered. Samples made with veil mats exhibited an intermediate amount of blistering while a 1-1/2 oz. of powder bound mat used in the resin rich backup layer showed superior blister resistance. As indicated earlier in this report sizing and binders can be considered a source of water soluble materials (WSM). This may be the cause of blistering in these samples. Samples of gun roving from different suppliers lost 1-6% by weight when they were heated to 700°C. However when these materials were immersed in water the pH of the water did not change substantially. Further work is necessary both in identifying this material and in using other reinforcement materials in the backup layer.

Preliminary results on the importance of an air inhibition layer at the gel coat laminate interface show that exposure of the gel coat to air while curing severely decreases blister resistance. Times between laying up the gel coat and the laminate of 0, 1 and 96 hrs. were used for a composite consisting of NPG isophthalic gel coat and a EG orthophthalic laminating resin (series 3, 32 and 34). Times of 1 hr. and 48 hrs. were used for series 95 and 93, respectively, which consisted of an NPG orthophthalic gel coats on an NPG/EG isophthalic laminating resin. In both cases the samples with long air exposure times blistered more quickly than those with shorter exposures. Series 11, which was made without a gel coat, developed tiny blisters soon after being immersed in the bath. However, these blisters disappeared in a short time. No further blistering was observed but crazing did develop. Series 7, which had the sequence of layup reversed so that the inner surface was not exposed to air but the outer layer was, did not develop blisters. However, the gel coat surface, which cured in air, became very chalky and appeared rough and pitted. the surface was similar to those described for the

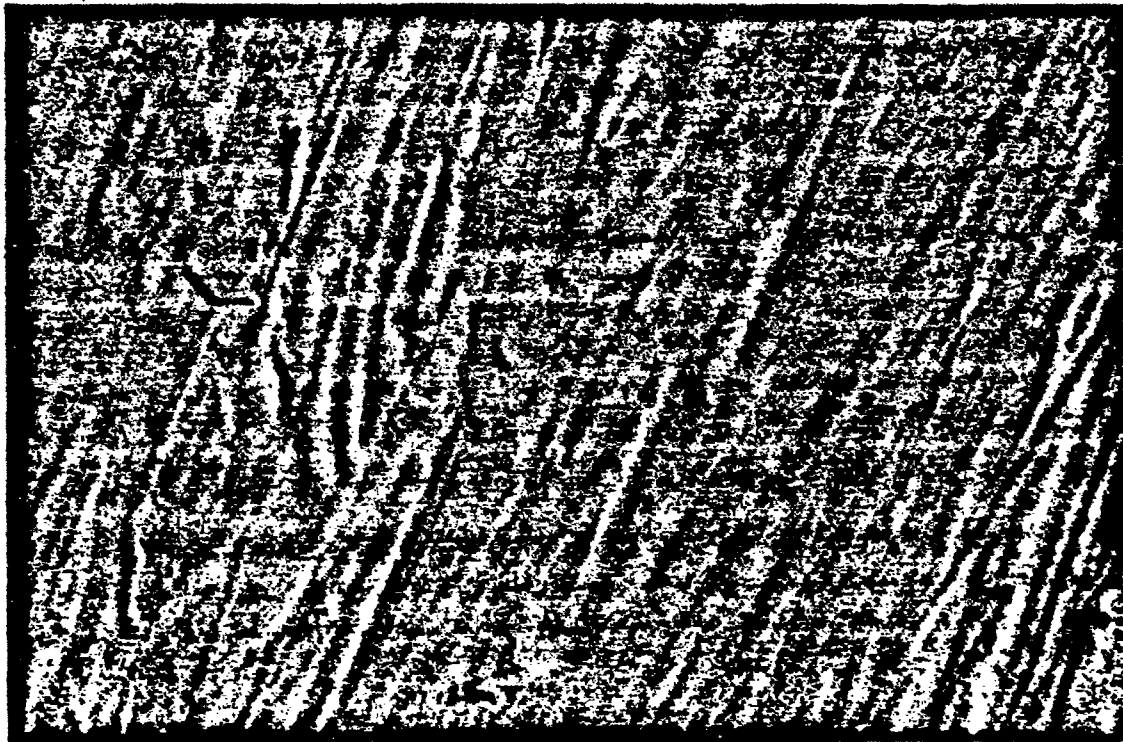


Figure 24 Surface of an orthophthalic gel coat cured against a waxed mold. This photograph was taken after 2000 hours of immersion in 65°C distilled water.

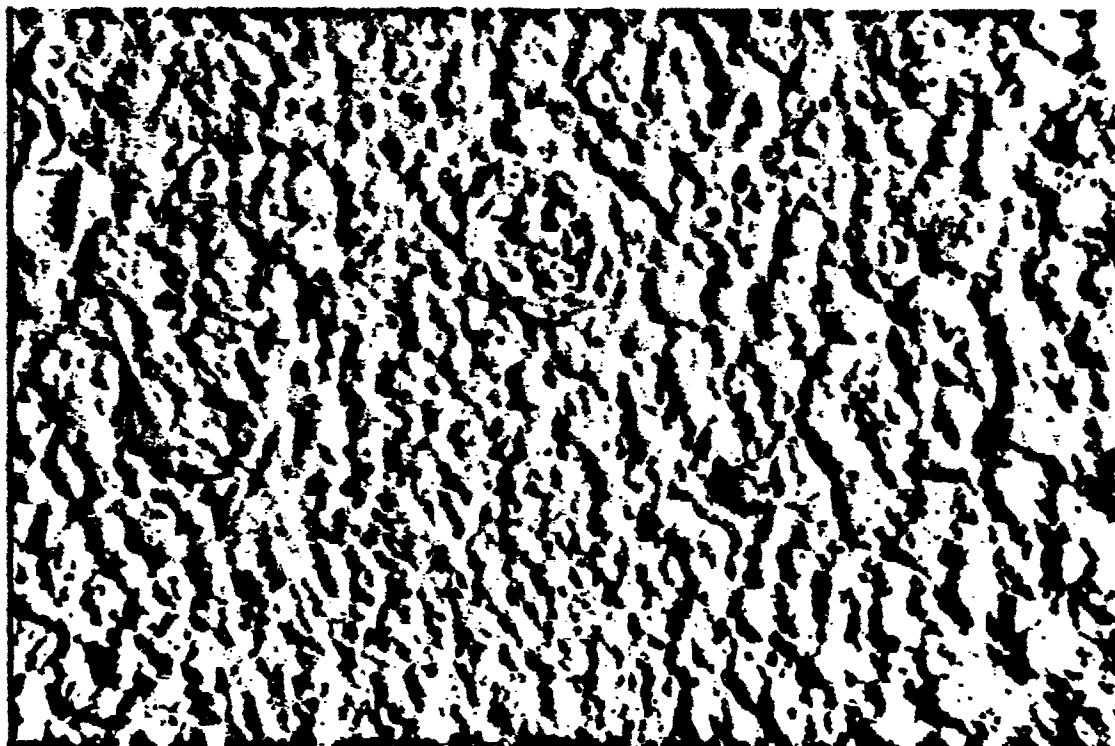


Figure 25 Surface of an orthophthalic gel coat cured in contact with air. This is the reverse side of the gel coat surface shown in figure 24. Exposure time approximately 2000 hours.

gel coat samples discussed below. The laminate surface, which was cured against the mold, did not blister but did develop many tiny cracks (crazing).

After 2,000 hours in the water bath, there is a major difference in the appearance of the air cured and non-air cured surfaces of the gel coat samples. Figure 24 shows the surface of this gel coat which was initially cured against a waxed mold. The surface appears smooth and unaffected by water. The opposite surface, cured in air under ambient conditions, is shown in Figure 25. This surface appears rough and pitted. The curing reaction, on this side was inhibited by oxygen reacting with free radicals near the surface. We feel the roughness is a result of water dissolving these degradation products from the surface. The absence of blistering in these materials may be related to the ability of WSM materials to leach out through the air inhibited surface during immersion. The reddish coloring on this surface is evidence that a material is leaching out in some area.

It is hypothesized that these air inhibition products dissolve in the laminating resin, creating a layer of water soluble materials directly underneath the gel coat. This material, then, serves as a site for blister initiation. Additional experiments are being conducted to explore this theory further.

Net weight change data indicates that the laminates reach a maximum weight after several hundred hours, and then begin to lose weight. In most cases, the samples eventually weighed less than they did when they were first immersed. The amount of weight gain and the time to maximum weight appear to be a function of the laminating resin and, to a lesser extent, the gel coat resin.

Generally, laminates made with PG orthophthalic laminating resin were found to gain more weight and to take longer to reach maximum weight than

those made from NPG/EG isophthalic laminating resins. The PG orthophthalic laminating resins with NPG orthophthalic gel coats gained more weight and took longer to reach a maximum weight than those with NPG isophthalic gel coats. EG orthophthalic laminating resins appear to gain more weight but reach a maximum in a shorter time than those constructed with PG orthophthalic laminating resin. However, when the gel coat cracks the laminates gained considerably more weight and took a longer time to reach the maximum. Since the laminating resin is the major polymer component in the panels, the amount of weight gain should be related to the equilibrium water content of the resin. This appears to be the case.

The maximum weight gain occurred much later than blister initiation. The maximum weight gain appears to occur about 2-3 times later than the time of blister initiation. For samples 3B and 7B, the initial rate of water uptake is about 3×10^{-5} g/cm² hr. this is about 10 times the initial rate of wt. loss of about 2×10^{-6} g/cm² hr.

Results from the exotherm temperature experiments indicated that the orthophthalic resin released less heat and did not get as hot as the isophthalic resins. It also indicated that the peak temperature was directly proportional to the ambient temperature of the layup. However the time to reach the peak temperature was an inverse function of the ambient temperature.

Finally, microscopic examination of thin cross-sections of blister samples indicated that concentrated water soluble materials may be a major factor in blister initiation time and severity. Microscopic examination of cross-sections of blisters indicated that they occur at disc cracks and in areas containing a concentration of water soluble material, such as promoter and sawdust. Pritchard (3,5,6) has reported that excess glycols in the laminate resin accelerate blistering. Bruggerman and Denoms (4) has reported

that water sensitive clays adversely affected blister resistance. To further test this idea we incorporated dyed sorbitol pellets in a layup. Large blisters appeared at these locations within the first day while general blistering did not occur for several days of immersion at 150op.

Disk cracks under the gel coat were observed in many samples after water immersion. These are due to swelling stresses produced by water absorption. A purple color (attributed to cobalt salts) was observed in some of these disk cracks. Stress birefringence caused by polymerization shrinkage at the gel coat laminate interface was observed under a polarized light microscope. Stress fields around and at the ends of glass fibers were also observed. Preliminary studies indicate that strain gauges can be used to measure the rate of stress buildup within the laminates. However more work is needed to be able to interpret the data that can be obtained.

Based on theory, data reported in the literature and the results of this research, a mechanism for blistering has been developed. This blister mechanism can be summarized by the following sequence of events:

1. When gel coat material is applied to the mold the outer surface is cured in the presence of air which produces an air inhibited layer containing large amounts of water soluble benzaldehydes.
2. When the laminating resin is applied, this water soluble material is dissolved in the first layer of the laminate.
3. As the laminating resin cures it bonds to the solid gel coat and then shrinks on curing producing a tensile stress in the laminate near the gel coat interface.
4. Upon immersion of a polyester laminate, water begins to diffuse into the polymer network.
5. This water absorption produces a swelling of the gel coat.

6. As the swollen layer tries to expand it produces tension in the underlying dry layer to which it is bonded.
7. This tensile field, which lies ahead of the advancing water front, produces stress which result in disk cracks in weak or brittle resin. The stress field is maximized by combination with polymerization stresses.
8. When the disk cracks open, they create a localized vacuum into which adjacent water soluble molecules can diffuse. The water soluble material produced by air inhibition is already present in this zone.
9. Diffusing water molecules reach the cracked zone and interact with the now concentrated water soluble material, forming a concentrated solution.
10. At this point the osmotic pressure begins. Water is drawn into the zone producing osmotic pressure which builds until the creep stress of the polymer is exceeded and a bubble begins to form in the gel coat.

The above sequence describes the relatively short term blistering which occurs just below the gel coat laminate interface where stress plays a role in nucleation. There is another type of blistering that occurs as a result of concentrated zones of water soluble material. For this type of blistering to occur, all that is necessary is that water reach the pocket of water soluble material. Such zones of materials may be present because of poor curing, under or over-catalyzation, poor mixing, poor housekeeping practices, water soluble binders or fillers, etc. A third type of blistering that may exist is one caused by prolonged water saturation of the polyester. Long term hydration of polyester may result in slow hydrolysis of ester linkages causing a blister which does not begin for several years. While field observations suggest the occurrence of this type of blisters, it has not been proven in laboratory.

Research should be continued on the effects of air inhibition, stress concentration, and glass binders. Boat manufacturers should consider using thicker gel coats, avoiding emulsion-type binders, preventing air inhibition of the gel coat and paying careful attention to quality control and assurance programs.

IV. SUMMARY

Listed below are the major findings of this research project. The reader is urged to consider the implications only after a thoughtful reading of the text.

1. Currently used glass reinforced polyester laminates are excellent materials for boat building but under some circumstances can develop blisters.
2. All resins contain some water soluble material (WSM). Only if this material is concentrated at a point in the hull it will cause blistering.
3. Blisters are caused by water diffusing into the hull and reacting with water soluble material to form a droplet of solution which, because of osmotic pressure, grows in volume and creates a force which deforms the overlying laminate and gel coat.
4. Three types of osmotic blisters occur. Water soluble material concentration blisters are formed from clusters of water soluble materials present in the hull when the boat is built. Stress induced blisters form because water soluble material is concentrated by water diffusion and stresses. Long term blisters form because of ester hydrolysis of the polyester molecules.
5. Other factors being equal, gel coat thickness determines when blisters will begin to form.
6. Laminate lay-up and post-cure temperatures did not have a major effect on blister initiation time or blister severity for temperatures between 50 and 90°F. Higher temperature postcure should improve laminate stability. The degree of cross-linking is a critical parameter since it determines the properties of a resin.

- 7 The resin-rich region between the gel coat and laminate must be carefully designed to minimizing blisters. The selection of the types of resin and glass are important factors. this includes compability of the resin with the gel coat resin and the type and amount of binder and size on the fiberglass.
8. Control of air inhibition during lay-up can improve blister resistance.
9. Microscopic examination of blisters indicated the presence of saw-dust, disk cracks, promoter and internal stresses in the region of the blister. Without such examination it is impossible to pin point the exact cause of blistering in a particular boat.
10. Leaching of material from gel coats will cause surface crazing of the material.
11. All samples blistered under the test conditions. The blister initiation time and severity of the blisters formed during this study was a function of both the laminating resin and the gel coat used. The types of glycol used in both resin also was an important factor. The size of the blisters depended on the length of time the sample is immersed, the laminating resin, the thickness and permeability of the gel coat and the temperature of layup and postcure. The chemistry of the materials are complex and variations were seen among generic types from different manufacturers.
12. It is recommended that boat manufacturers institute programs of quality control and quality assurance, with specification for their supplies to minimize the blister problem. Standardized test procedures would help comparison and interpretation of data. Procedures used to make and postcure the samples should be similar to those used in manufacturing. This will permit comparison of different resins and will more accurately reflect blister potential in actual use.

Notation

C	Water concentration (moles H ₂ O/volume)
D	Polyester-water diffusion coefficient (Length ² /time)
EG	Ethylene glycol
IPA	Isophthalic acid
WSM	Low molecular weight water soluble material
NPG	Neopentyl glycol
OPA	Orthophthalic acid
PG	Propylene glycol
MEKP	Methyl ethyl ketone peroxide
S.	Solubility of water
t	Time parameter
x	Distance parameter

References

1. Fraser-Harris, A.B.F., and J.H. Kyle. "FRP bottom blistering." Paper presented at the Chesapeake Sailing Yacht Symposium, Annapolis, Md., January 15, 1983.
2. Repairs to Blisters in Glass Fibre Hulls. British Plastics Federation, Report No. 244/1.
3. Davis, R., J.S. Ghortra, T.R. Malhi, and G. Pritchard. "Blister formation in RP: the origin of the osmotic process." 38th Annual Conference, SPI Reinforced Plastics/Composites Institute, Paper 17-B, 1983.
4. Brueggeman, W.H., and S.D. Denoms. "Blistering in coated reinforced plastic laminates exposed to water." 38th Annual Conference, SPI Reinforced Plastics/Composites Institute, Paper 17-C, 1983.
5. Abeysinghe, H.P., J.S. Ghortra, and G. Pritchard. "Substances contributing to the generation of osmotic pressure in resins and laminates." Composites, 1983, p. 57.
6. Abeysinghe, H.P., W. Edwards, G. Pritchard, and G.J. Swampillai. "Degradation of cross-linked resins in water and electrolyte solutions." Polymer 23, 1982, p. 1785.
7. Brueggeman, W.H. "Blistering of gel coat laminates." 34th Annual Conference, SPI Reinforced Plastics/Composites Institute, Paper 6-A, 1979.
8. Adams, R.C., "Variables influencing the blister resistance of marine laminates." 37th Annual Conference, SPI Reinforced Plastics/Composites Institute, Paper 21-B, 1982.
9. Birely, A.W., J.V. Dawkins and H.E. Strauss, "Blistering in Glass Fibre Reinforced Polyester Laminates." British plastics Federation, 14th Reinforced Plastics Congress, 1985.
10. Norwood, L.S., D.W. Edgell, and A.G. Hankin. "Blister performance of GRP systems in aqueous environments." 36th Annual Conference, SPI Reinforced Plastics/Composites Institute, Paper 23-F, 1981.
11. Edwards, H.R. "Variables influencing the performance of a gel coated laminate." 34th Annual Conference, SPI Reinforced Plastics/Composites Institute, Paper 4-D, 1979.
12. Crump, Scott. "A Study of Blister Formation in Gel Coated Laminates". 41st Annual Conference, Reinforced Plastics/Composites Inst., SPI, Paper 13-C, 1986.
13. Rath, Dick. "Fiberglass Blistering", Yachting, p. 84, April, 1985.
14. Discussions at ABBRA Meetings, Spring, 1984, 1985, 1986.
15. Boenig, H.V. Unsaturated Polyesters: Structure and Properties, Elsevier, Amsterdam, 1964.

16. Bird, R.E., W.E. Stewart, and E.N. Lightfoot. Transport Phenomena, 7th printing, Wiley, New York, 1960.
17. Treybal, R.E., Mass Transfer Operations, 3rd ed., McGraw-Hill, Inc., 1980.
18. Ashbee, K.H.G., F.C. Frank, and R.C. Wyatt. "Water damage in polyester resins." Proc. Roy. Soc. A300, 1967, p. 415.
19. Ghotra, J.S. and Geoffrey Pritchard, Osmotic Blister Formation and Prevention in FRP Marine Laminates, Proc. 28th Natl. SAMPE Symp., 1983, p. 807.
20. O'Toole, J.L., "Design Guide for Plastics". Modern Plastics Encyclopedia, Vol. 61, McGraw-Hill, 1985, p. 425.
21. Norwood, L.S., "Recent developments in Polyester Matrices and Reinforcement for Marine Applications, in particular polyester/Kevlar composites." Paper 6, Port and Coast Services Conference, U.K., 1980.
22. Noller, D.C., S.L. Stengel and O.L. Mageli. "Effect of accelerators and inhibitors on peroxide curing polyesters." Modern Plastics, 1962.